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13. SUPPLEMENTARY NOTES

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14. ABSTRACT

Final Progress: 01 Jun 2002 to 30 Jun 2003

The DCP process has been used to synthesize very-high-melting, lightweight tungsten/carbide or tungsten/boride composites via conversion reactions of the following type: $(M) + WX(s) = MX(s) + W(s)$ (1) where (M) is a reactive element dissolved within a Cu-bearing melt, and WX and MX are ceramic reactant and product phases, respectively. Reactions leading to ZrC/W, TiC/W, HfC/W, and ZrB₂/W composites at < 1300°C have been demonstrated. Conversion reactions leading to ZrC/W and HfC/W composites proceeded via the formation of a layer of ZrC or HfC on a layer of W that, in turn, formed on the WC reactant particles. Hence, upon complete reaction, the sizes and distributions of the carbide and tungsten products were directly related to the sizes and distributions of the WC reactant particles. Conversion reactions leading to ZrB₂/W and TiC/W composites proceeded via the formation of discrete ZrB₂ or TiC particles in the melt, so that the sizes and distributions of these product phases were not highly correlated to the sizes and distributions of the WB and WC reactant particles, respectively. Porous WC

15. SUBJECT TERMS

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AFOSR Final Performance Report

Project Title: Lightweight, Robust, & Low Cost Carbide/Tungsten Composites in Near Net Shapes for Advanced Solid-Fueled Rocket Nozzles for the IHRPT Program

Award Number: F49620-02-1-0349

Start Date: June 1, 2002

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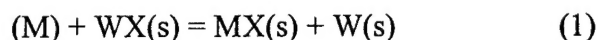
*This research was conducted while the PI was a faculty member at The Ohio State University.

Objective:

The objectives of this project have been: i) to evaluate the influence of processing conditions in the DCP (Displacive Compensation of Porosity) method on the microstructures of the resulting tungsten/carbide composites, and ii) to fabricate nozzle-shaped tungsten/carbide composites by the reactive infiltration of porous carbide preforms.

Approach and Key Results:

The DCP process has been used to synthesize very-high-melting, lightweight tungsten/carbide or tungsten/boride composites via conversion reactions of the following type:



where (M) is a reactive element dissolved within a Cu-bearing melt, and WX and MX are ceramic reactant and product phases, respectively. Reactions leading to ZrC/W, TiC/W, HfC/W, and ZrB₂/W composites at $\leq 1300^\circ\text{C}$ have been demonstrated. Conversion reactions leading to ZrC/W and HfC/W composites proceeded via the formation of a layer of ZrC or HfC on a layer of W that, in turn, formed on the WC reactant particles. Hence, upon complete reaction, the sizes and distributions of the carbide and tungsten products were directly related to the sizes and distributions of the WC reactant particles. Conversion reactions leading to ZrB₂/W and TiC/W composites proceeded via the formation of discrete ZrB₂ or TiC particles in the melt, so that the sizes and distributions of these product phases were not highly correlated to the sizes and distributions of the WB and WC reactant particles, respectively.

Porous WC preforms with hourglass shapes (for rocket nozzle liners) were produced by gel casting (via collaboration with Dr. J. R. Schorr and Mr. P. J. Wurm of MetaMateria Partners). The porous preforms were exposed to molten Zr₂Cu at 1200-1300°C and ambient pressure. The Zr₂Cu liquid rapidly infiltrated into the preforms and underwent a displacement reaction with the WC to yield the solid products, ZrC and W. The performance of a DCP-derived, ZrC/W-based nozzle insert in a Pi-K rocket motor test was examined at Edwards Air Force Base (via collaboration with Dr. Wes Hoffman and Dr. P. G. Wapner).

Conclusions:

Composites of ZrC/W, TiC/W, HfC/W, and ZrB₂/W have been synthesized at $\leq 1300^\circ\text{C}$ at ambient pressure by this pressureless reactive infiltration process. The DCP process enables such ultra-high-melting ceramic/refractory metal composites to be fabricated in complex and near net shapes without the need for high-temperature or high-pressure densification or for extensive machining (i.e., relatively expensive processing steps are avoided). The increase in internal solid volume associated with the displacement reactions of this process resulted in a filling of the prior pore spaces of the preforms ("displacive compensation of porosity"), so that dense composites were produced. Because the preforms remained rigid during reactive infiltration, the final DCP-derived composites retained the external shapes and dimensions of the starting preforms.

To generate ZrC/W-based rocket nozzle liners, gel-cast WC preforms in the shape of an hourglass were infiltrated and reacted with a Zr-Cu melt at 1200-1300°C and ambient pressure. The resulting ZrC/W-based composites were dense and retained the hourglass shape of the starting WC preforms. A DCP-derived, ZrC/W-based nozzle liner was found to be resistant to the severe thermal shock and erosive conditions of a Pi-K solid-fueled rocket motor test conducted at Edwards Air Force Base.

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Final Project Report


"Lightweight, Robust, & Low Cost Carbide/Tungsten Composites in Near Net Shapes for Advanced Solid-Fueled Rocket Nozzles for the IHPRPT Program"

Project Award No. F49620-02-1-0349

Air Force Office of Scientific Research

Project Duration: June 1, 2002 to June 30, 2003
(with no-cost extension)

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Incongruent reduction of tungsten carbide by a zirconium-copper melt

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The reduction of tungsten carbide (WC) to elemental tungsten by reaction with a Zr-Cu melt was examined. Dense WC disks were immersed in a vertical orientation in molten Zr_2Cu at 1150–1400 °C for 1.5–24 h. Continuous, adherent layers of W and ZrC formed at WC/melt interfaces. The rates of thickening of the W and ZrC product layers were examined as a function of reaction time and temperature and position along the vertical WC surface. Such kinetic data, along with microstructural analyses, indicate that the incongruent reduction of tungsten carbide is likely to be controlled by carbon diffusion through one or both of the product layers.

I. INTRODUCTION

Composite materials comprised of refractory metals (e.g., W, Mo, Ta, Re) and carbides (e.g., HfC, ZrC, TiC, TaC) can possess attractive combinations of chemical, thermal, and mechanical properties.^{1–9} Such composites can have higher hardness, greater resistance to wear and creep, and reduced weight relative to refractory metals, and can also exhibit higher fracture strengths, higher toughnesses, and improved thermal shock resistance relative to monolithic carbides. Hence, these materials can be attractive for a variety of applications in the aerospace/aircraft, automotive, energy production, materials processing, defense, and other industries.^{7–11}

Among the most extreme environments in aerospace applications can be found in the throat regions of solid-fueled rockets, where combustion products can exceed 2500 °C and flow at supersonic velocities.^{9,10} Although refractory metals, such as W and Re ($T_m[\text{W}] = 3422$ °C, $T_m[\text{Re}] = 3186$ °C), may be used under such conditions, these materials possess high specific densities ($\rho[\text{W}] = 19.3 \times 10^3$ kg/m³, $\rho[\text{Re}] = 21.0 \times 10^3$ kg/m³).^{9,12,13} Refractory metal/carbide composites, such as W/ZrC composites, can be attractive alternatives to pure refractory metals. A composite comprised of equal volumes of W and ZrC is 33% lighter than pure W (12.9×10^3 versus 19.3×10^3 kg/m³).¹³ Such composites are also thermally, chemically, and mechanically compatible. Unlike most

metal/ceramic composites, the average linear thermal expansion coefficients of W and ZrC are similar at 20 °C ($4.5 \times 10^{-6}/\text{K}$ versus $4.0 \times 10^{-6}/\text{K}$, respectively) and at 2700 °C ($9.2 \times 10^{-6}/\text{K}$ versus $10.2 \times 10^{-6}/\text{K}$, respectively).^{4,5} As a result, W/ZrC composites have exhibited excellent resistance to thermal shock at surface heating rates of ≈ 2000 °C/s.⁸ Like tungsten, zirconium carbide melts at a high temperature (i.e., up to 3445 °C).³ ZrC and W exhibit limited mutual solid solubilities and do not form intermediate compounds.³ ZrC can endow a co-continuous W/ZrC composite with enhanced resistance to high-temperature creep and erosion, whereas W can act as a ductile reinforcement at high temperatures for enhanced toughness.^{2,6–8}

Dense, co-continuous W/ZrC composites have been produced by the hot pressing of powder mixtures.^{7,8} However, the high temperatures (≥ 2000 °C) and pressures, along with subsequent machining required to generate more complex, nonaxisymmetric shapes, render such processing relatively expensive. An attractive alternative to such conventional processing is the displacive compensation of porosity (DCP) method.^{14–17} The DCP method involves the reactive infiltration of a metallic liquid into a rigid, porous, ceramic-bearing preform at ambient pressure. The liquid undergoes an incongruent reduction reaction with a ceramic phase in the preform to yield a ceramic product of larger volume. (Note: Incongruent reduction occurs when a solid ceramic is converted by reduction into solid and liquid products of different composition than the original solid ceramic.¹⁸) If the starting porous preform is rigid (i.e., consists of a continuous network of necked particles), then the external shape and dimensions of the preform are retained as the internal pore spaces become filled. The DCP process has recently been used to produce W/ZrC-bearing composites.¹⁵ Molten Zr_2Cu was infiltrated into rigid, porous

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WC preforms, whereupon the Zr_2Cu reacted with WC to yield solid ZrC and W, along with a Cu-rich liquid. Dense, near-net-shaped W/ZrC-bearing composites were generated at only 1200–1300 °C.

Although dense, near-net-shaped refractory metal/carbide composites have been fabricated by the DCP method, the kinetic mechanisms of incongruent reduction are not well understood. The purpose of this paper is to determine the rate-limiting step(s) associated with the incongruent reduction of dense tungsten carbide WC by reaction with molten Zr_2Cu at 1150–1400 °C.

II. EXPERIMENTAL

Incongruent reduction experiments were conducted by immersing dense disks of WC into a molten bath of Zr_2Cu . Dense WC disks were prepared by hot isostatic pressing of WC powder. The WC powder possessed an average particle size (d_{50}) of 0.88 μm and a purity of >99.5% (Alfa Aesar, Johnson Matthey, Ward Hill, MA). The WC powder was mixed with 3 wt.% of an aqueous 10 wt.% solution of polyvinyl alcohol and then uniaxially pressed into disks (13 mm in diameter, ≈ 3 mm in thickness) at a peak stress of 3×10^8 Pa. The green disks were heated for 4 h at 400 °C in flowing argon, to remove the polyvinyl alcohol, and then for 4 h at 1400 °C. The specimens were further heated for 1 h at 1850 °C under an argon pressure of 7×10^4 Pa, and then hot isostatically pressed at an argon pressure of 2.1×10^8 Pa at 1850 °C for 1 h. The WC disks were polished using a series of SiC abrasive papers and diamond pastes to a surface finish of 0.25 μm . To reveal the grain structure, polished WC cross sections were thermally etched at 1400 °C for 4 h in flowing argon. The argon gas used at the various stages of processing discussed above was passed through a titanium getter (Oxy-gon Industries, Epsom, NH), so that the oxygen partial pressure was reduced to $\leq 3 \times 10^{-5}$ Pa.

Zr_2Cu was prepared using Zr sponge (99.6% purity, 0.8–19 mm pieces, Johnson-Matthey) and Cu pieces (99.99% purity, ≈ 1 mm diameter, Atomergic Chemetals, Farmingdale, NY) as precursors. These materials were placed within a magnesia crucible and heated to 1300 °C for 4–8 h in an oxygen-gettered argon atmosphere. The resulting ingot was crushed into pieces of a few millimeters in diameter and then remelted under similar conditions. X-ray diffraction (XRD) analyses confirmed that the final ingots were comprised of Zr_2Cu .

Prior to an immersion experiment, the hot-isostatically-pressed WC disks were positioned vertically within a magnesia holder inside a magnesia crucible, as shown in the schematic of Fig. 1(a). The disk was surrounded by solid pieces of Zr_2Cu . For each experiment, the molar ratio of Zr_2Cu to WC within the crucible was

18 ± 1 . After purging the furnace with flowing, oxygen-gettered argon for 1 h, the furnace was heated to the target temperature (in the range of 1150–1400 °C) and held for a time ranging from 1.5 to 24 h. After cooling, the WC specimens, along with adjacent, adherent solidified melt, were cross sectioned and polished to a surface finish of 0.25 μm . For each reaction temperature and time, the average thicknesses of product layers formed at WC/Zr–Cu interfaces were evaluated by dividing the area of each product layer, obtained by image analyses (3.0.027 software, Clemex Vision, Langueuil, Quebec, Canada) of backscattered electron images, by the length of the interface.

III. RESULTS

After hot isostatic pressing, the tungsten carbide specimens possessed bulk densities of $15.55 (\pm 0.08) \times 10^3 \text{ kg/m}^3$, which corresponded to $99.2 \pm 0.5\%$ of the theoretical value for WC ($15.67 \times 10^3 \text{ kg/m}^3$). XRD analysis, and a secondary electron image of a thermally etched cross-section of a hot-isostatically-pressed WC specimen, are shown in Figs. 2(a) and 2(b), respectively. The XRD pattern revealed predominant diffraction peaks for hexagonal WC. Diffraction peaks for $\alpha\text{-W}_2\text{C}$ or graphite (for C-poor or C-rich compositions, respectively) were not detected, although a trace amount of a cubic WC_{1-x} phase may have been present.¹³ Secondary electron images of etched cross sections revealed dense WC specimens with an average grain size of 1.5 μm .

Backscattered electron images of polished cross sections of a specimen exposed to molten Zr_2Cu for 1.5 h at 1400 °C are shown in Fig. 1(b). For each cross section, a relatively bright reaction product layer was observed adjacent to the unreacted WC. This bright layer was separated from the solidified Zr_2Cu by a relatively dark product layer. Energy dispersive x-ray analyses indicated that the relatively bright layer was comprised of tungsten, whereas the dark layer was comprised of zirconium carbide. Examination of similar cross sections obtained from other specimens revealed that the W and ZrC product layers forming on WC increased in thickness as a function of exposure time to the Zr_2Cu melt. The squares of the average W and ZrC layer thicknesses are plotted against reaction time in Figs. 3(a) and 3(b). For each reaction temperature, the data points exhibited a good fit to parabolic kinetics. The cross sections shown in Fig. 1(b) were obtained from locations near the top and bottom of the vertically oriented specimen, respectively [Fig. 1(a)]. The average thicknesses of the W and ZrC layers formed at the top and bottom locations were similar. The thicknesses of product layers formed at other temperatures and times were also observed to be independent of vertical position along the specimen surfaces.

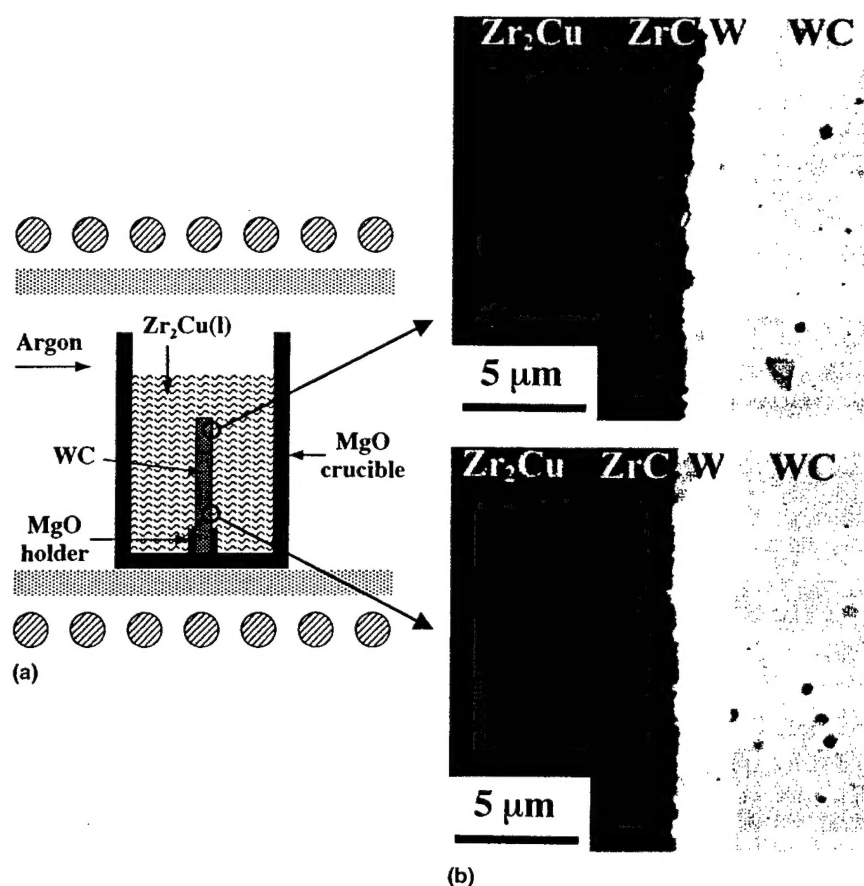


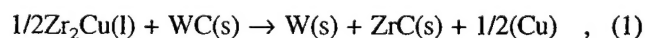
FIG. 1. (a) Experimental setup for the immersion of dense WC disks in molten Zr_2Cu . (b) Backscattered electron images of polished cross sections of dense WC after reaction with molten Zr_2Cu for 1.5 h at 1400 °C. These images were obtained at various locations along the surface of the vertically immersed WC specimens, as shown in the schematic.

The slopes of the lines shown in Figs. 3(a) and 3(b) were used to obtain the parabolic rate constants (K_p values) for the thickening of the tungsten and zirconium carbide layers at each reaction temperature.¹⁹ The logarithms of the parabolic rate constants are plotted against the inverse of temperature in Fig. 4. For each product layer, the data points exhibited a good fit to Arrhenius behavior. The activation energies, obtained from the slopes of these lines, were virtually the same for the growth of the tungsten (263 kJ/mol) and zirconium carbide (247 kJ/mol) layers.

For immersion times up to 24 h at temperatures of 1150–1400 °C, continuous layers of W and ZrC tended to form on the WC specimens. However, infrequent, isolated discontinuities in the zirconium carbide layer resulted in the exposure of the tungsten layer to the zirconium-bearing melt, as shown in Fig. 5. Enhanced consumption of the WC specimen was observed (i.e., pits formed in the WC) at these locations [Fig. 5(c)]. Within these pits, the thickness of the tungsten layer was locally reduced, and discontinuous particles of W_2Zr formed [Figs. 5(b) and 5(c)].

IV. DISCUSSION

Exposure of dense WC specimens to molten Zr_2Cu at 1150–1400 °C resulted in the following net incongruent reduction reaction:



where (Cu) refers to copper dissolved within the excess liquid solution surrounding the specimen. This reaction is strongly favored from a thermodynamic perspective. For example, a thermodynamic calculation using available data for the excess Gibbs free energy of mixing of Zr–Cu melts, and the free energies of formation of ZrC and WC, indicated that this reaction should occur spontaneously at 1300 °C for Zr–Cu melts with >0.092 at.% Zr (i.e., only 920 ppm Zr was required in the melt).^{20–22} For the immersion of WC into molten Zr_2Cu at 1300 °C, the Gibbs free-energy change for Reaction (1) was calculated to be –135.2 kJ/mol.^{20–22}

A corrosion process is generally considered to be “passive” if a continuous, adherent, solid product layer forms on the corroding solid surface, so as to physically separate the corroding solid from the reactive fluid and

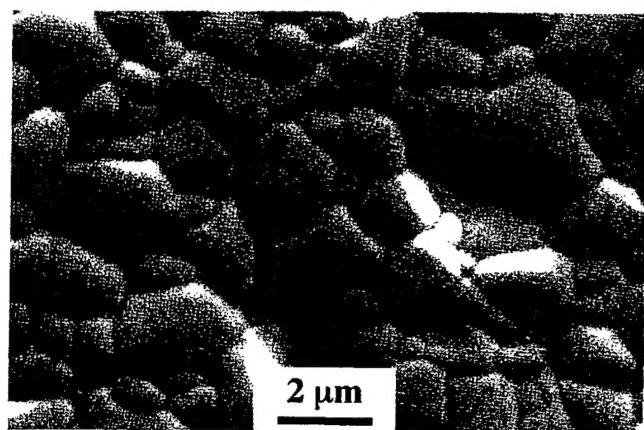
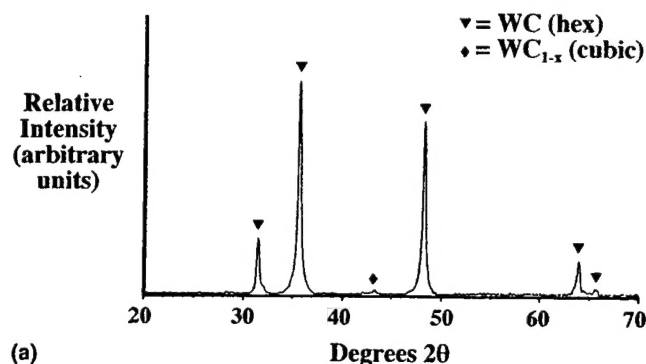
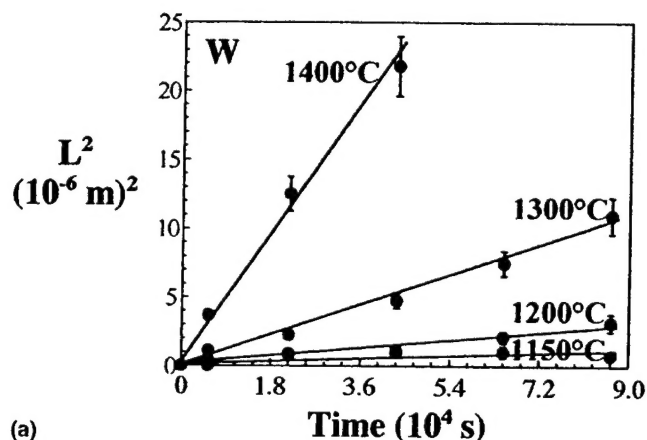


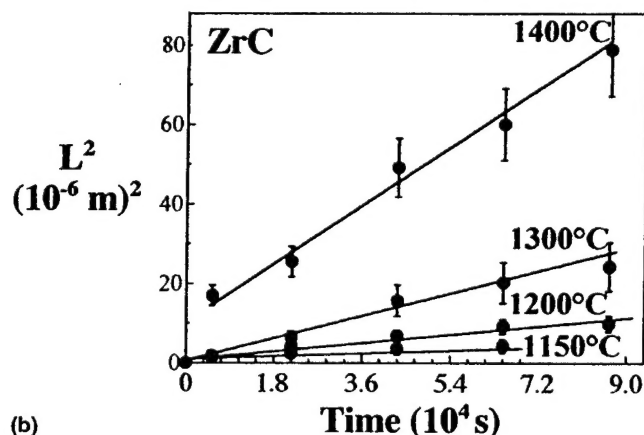
FIG. 2. (a) XRD analysis of a hot isostatically pressed WC specimen. (b) Secondary electron image of a thermally etched cross section of a hot isostatically pressed WC specimen.

thereby slow the rate of corrosion.²³ In the present work, the W and ZrC products of Reaction (1) generally formed as continuous, adherent layers on the underlying dense WC. By analogy to other types of corrosion, such ZrC and W layer formation on WC may be considered to be an example of "passive incongruent reduction." At locations where the ZrC layer was not continuous, the underlying W layer reacted with the melt to form discontinuous particles of W_2Zr (Fig. 5). At these locations, the rate of consumption of the WC was locally enhanced, so that pits formed on the specimen surface [Fig. 5(c)]. Such accelerated reaction due to the formation of discontinuous (and apparently less protective) ZrC and W_2Zr products is an example of "active incongruent reduction."

During passive incongruent reduction in molten Zr_2Cu , the WC was physically separated from the melt by layers of W and ZrC. In the present experiments, excess amounts of the reactants, $Zr_2Cu(l)$ and $WC(s)$, were used to avoid depletion of these reactants during the course of a given experiment. For example, under the most extreme reaction condition of 1400 °C for 24 h, less than 0.03 at.% of the zirconium available in the melt, and less than 0.9 at.% of the carbon available in the WC



(a)



(b)

FIG. 3. Plots of the square of the layer thickness L^2 versus reaction time for the (a) W and (b) ZrC product layers formed on WC upon immersion in $Zr_2Cu(l)$ at 1150–1400 °C.

specimen, were consumed to produce the ZrC and W layers. Under these conditions, the rate of passive incongruent reduction of WC could have been limited by one or more of the following steps: (i) solid-state diffusion (through the WC specimen, or through the W or ZrC product layers), (ii) liquid phase diffusion, (iii) a chemical reaction (at the WC/W, W/ZrC, or ZrC/melt interfaces).

The formation of W and ZrC layers on planar WC specimens during immersion in molten Zr_2Cu resulted in very little change in the surface area of the planar WC specimens ($\leq 0.3\%$). As seen in Figs. 3(a) and 3(b), the tungsten and zirconium carbide layers increased in thickness at parabolic rates for all of the temperatures examined. Such parabolic kinetics are not consistent with chemical reaction control; that is, with essentially constant interfacial areas and reactant concentrations, chemical reaction control should have resulted in linear kinetics.¹⁹

The parabolic rate constants for the thickening of the tungsten and zirconium carbide layers followed Arrhenius behavior (Fig. 4). The similar values of activation energy obtained for W and ZrC layer growth (263 and

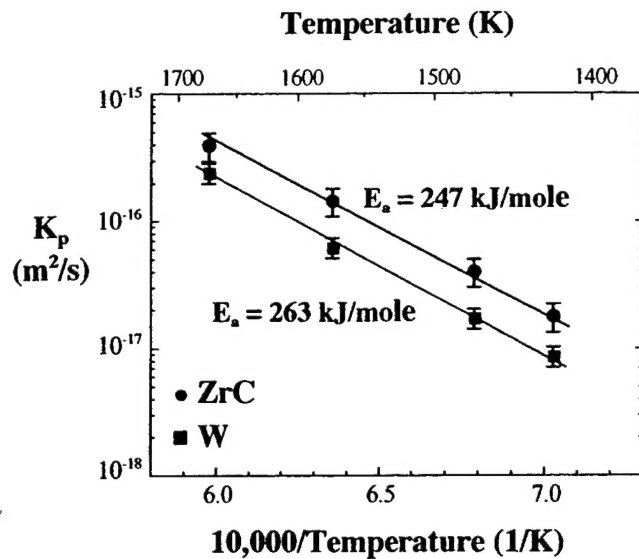
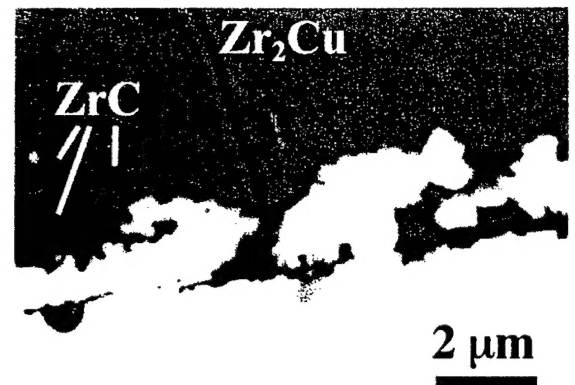


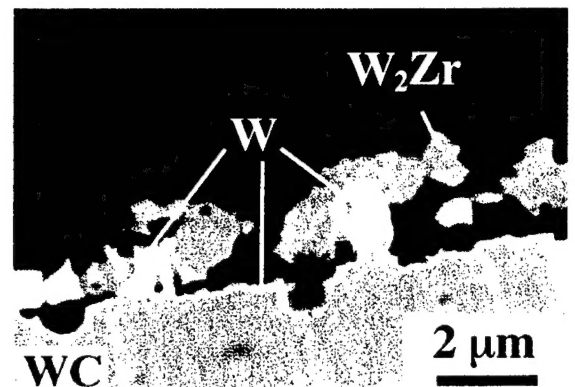
FIG. 4. Plot of the parabolic rate constants K_p for thickening of the W and ZrC product layers as a function of inverse temperature (E_a = activation energy).

247 kJ/mol, respectively) suggested that the steady-state growth of both layers was controlled by a common mechanism. These activation energies were considerably higher than values reported for the diffusion of copper or zirconium in molten copper or in Zr-Cu-bearing liquids.^{24,25} Furthermore, a change in the melt density near the WC/melt interface, due to the selective removal of zirconium from the melt by Reaction (1), should have resulted in convection in the melt. If liquid-phase diffusion was the rate-limiting step, then such density-driven free convection in the vicinity of a vertical plate should have led to a steady-state reaction rate that was independent of time, but dependent on vertical position.²⁶ However, the present results indicated that the product layer thickening rates were independent of position [Fig. 1(b)] and dependent on time (Fig. 3). Hence, mass transport through the liquid is unlikely to be the rate-limiting step.

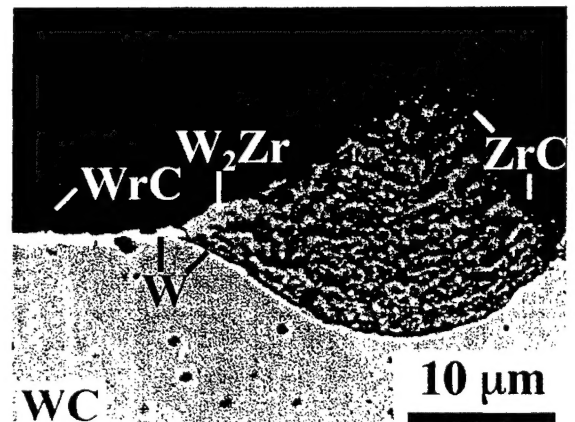
Activation energies reported for diffusion through WC, W, and ZrC are shown in Table I.²⁷⁻³² The activation energies reported for the lattice diffusion of zirconium and carbon through ZrC (719 and 473 kJ/mol, respectively^{27,28}) were significantly higher than the values obtained in the present work. However, the activation energies associated with the diffusion of carbon (Table I) along grain boundaries in WC and ZrC, or through the lattice of tungsten, agreed reasonably well with the values shown in Fig. 4.²⁸⁻³¹ At locations where the ZrC layer was not continuous, the WC was observed to undergo an enhanced rate of reaction [i.e., a pit formed in the WC specimen, as shown in Fig. 5(c)]. At such regions of active incongruent reduction, the thickness of the tungsten layer was locally reduced and discrete particles of W_2Zr formed. Such enhanced local reaction (pitting)



(a)



(b)



(c)

FIG. 5. (a,b) High-magnification backscattered electron images revealing the formation of W_2Zr particles at locations where the ZrC product layer was not continuous. (Note: two images of the same location are shown with different contrasts to reveal the ZrC, W, and W_2Zr phases.) (c) A lower magnification backscattered electron image, relative to (a) and (b), revealing the formation of a pit in the WC surface. Appreciable W_2Zr particle formation is observed in the vicinity of the pit.

should not have occurred if carbon diffusion through the tungsten carbide was rate limiting. Hence, these results indicate that the rate-limiting step for the passive incongruent reduction of tungsten carbide is likely to be the

TABLE I. Activation energies (kJ/mol) reported for grain boundary (GB) or lattice diffusion of carbon (C^{14}) and zirconium (Zr^{95}) through WC, W, and ZrC.²⁷⁻³²

| C^{14} | | | | | | Zr^{95} |
|----------|---------|-----|---------|---------|---------|-----------|
| WC | | W | | ZrC | | ZrC |
| GB | Lattice | GB | Lattice | GB | Lattice | Lattice |
| 297 | 368 | 169 | 207 | 288-376 | 473 | 719 |

solid-state diffusion of carbon through the lattice of the tungsten product layer and/or through grain boundaries in the zirconium carbide product layer.

V. CONCLUSIONS

The exposure of dense, vertically oriented disks of WC to molten Zr_2Cu at 1150–1400 °C for 1.5–24 h resulted in the formation of continuous, adherent layers of W and ZrC on the WC surface. The effects of time, temperature, and vertical position on the thickening rates of the W and ZrC product layers, and the influence of infrequent disruptions in these product layers on the local WC consumption rate, indicate that the passive incongruent reduction of WC is likely to be controlled by solid-state diffusion of carbon through the lattice of the W layer and/or through grain boundaries in the ZrC layer.

ACKNOWLEDGMENTS

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**THE FABRICATION OF DENSE, W-RICH, W/ZrC COMPOSITES
BY THE PRIMA-DCP PROCESS AT 1300°C**

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ABSTRACT

ZrC/W composites can be attractive for applications requiring ablation resistance, creep resistance, and strength at extremely high temperatures ($\geq 2000^\circ\text{C}$). The PRIMA-DCP process is a novel, rapid, and near net-shape method that is an attractive alternative to conventional hot pressing of dense carbide/refractory metal composites. In this paper, the PRIMA-DCP process has been used to produce dense W/ZrC-bearing composites containing appreciable tungsten (>40 vol%). Porous, rigid W_2C preforms were infiltrated (pressureless) with a Zr-Cu liquid at 1300°C . Zr in the liquid underwent a displacement reaction with W_2C to yield ZrC and W. Because the total volume of the solid ZrC and W products was larger than the volume of the solid reactant, W_2C , the prior pores in the rigid preform became filled with these solid products. Such reaction-induced densification caused the residual, inert Cu-rich liquid to be largely squeezed out of the reacting body. Thus, copper acted as an ideal transient processing agent, by lowering the reactive infiltration temperature (e.g., the melting point of Zr_2Cu is about 800°C lower than for pure Zr) and then subsequently leaving the specimen after reactive conversion. The effects of processing parameters on the phase content and microstructure of the formed composite materials are discussed.

INTRODUCTION

Tungsten metal has recently attracted interest as a reinforcement phase in high-temperature composite materials, such as superalloy matrix composites reinforced with high strength tungsten wire [1]. Co-continuous, interpenetrating composites containing a network of tungsten can also exhibit attractive properties (e.g., isotropic mechanical behavior) [2]. Tungsten/copper or tungsten/silver composites produced by infiltration of molten copper or silver, respectively, into a porous, rigid tungsten preform (prepared by the partial sintering of tungsten powder at temperatures up to 2200°C) are examples of such

co-continuous composites [2,3]. The high-temperature strength and thermal shock resistance of such infiltrated tungsten materials has led to their use in extremely high temperature environments, such as nozzle throat liners and rudders in aluminum-based, solid-fuel rockets [2,3]. The low-melting copper and silver phases possess relatively high boiling points (e.g., Cu melts at 1084.9°C and boils at 2562°C [4]) and, much like the cooling of human skin by sweating, serve to remove heat from the engine component by transpirative cooling. Although these infiltrated tungsten composites have found application in underwater launched ballistic missiles [2], such composites suffer from a degradation of strength at very high temperatures ($\geq 2000^\circ\text{C}$ [5]) and exhibit excessive weights (i.e., tungsten possesses a density of 19.3 g/cm^3) [6].

Tungsten-bearing composites with stiff, creep-resistant, and lightweight carbide reinforcements can be attractive alternatives to W/Cu or W/Ag composites. Consider, for example, composites of tungsten with zirconium carbide. Zirconium carbide is thermally well-suited for use with tungsten. Zirconium carbide possesses a comparably high melting temperature (up to 3420°C [7]). Furthermore, unlike W/Cu, W/Ag, or most ceramic-metal composites, the linear coefficients of thermal expansion of ZrC and W are well matched (ranging from $4.0 \times 10^{-6}/^\circ\text{C}$ to $10.2 \times 10^{-6}/^\circ\text{C}$ and $4.5 \times 10^{-6}/^\circ\text{C}$ to $9.2 \times 10^{-6}/^\circ\text{C}$, for ZrC and W, respectively, from room temperature to 2700°C [8,9]). As a result, composites of tungsten and zirconium carbide have exhibited excellent resistance to thermal shock; for example, W/ZrC composites have survived temperature changes of up to 2000°C per second [5]. Zirconium carbide is also mechanically well-suited for inclusion within tungsten composites. Co-continuous tungsten/carbide composites should exhibit enhanced high-temperature stiffness and hardness relative to monolithic tungsten, while also retaining high toughness due to the ductility of tungsten (for temperatures in excess of the ductile-to-brittle transformation temperature of tungsten; that is, above 400°C) [2,10]. Indeed, tungsten-matrix composites containing 20-30 vol% zirconium carbide have recently been reported to exhibit high strengths at elevated temperatures (e.g., $>900\text{ MPa}$ at 1200°C) and excellent resistance to ablation [5,11]. Carbide-reinforced refractory metal or intermetallic phase composites have also exhibited enhanced creep resistance relative to the monolithic counterparts (particularly above the recrystallization temperatures of the metal or ordered intermetallic) [7,12]. Finally, zirconium carbide is chemically compatible with tungsten. No additional compounds form between W and ZrC, and these phases exhibit limited mutual solid solubility at elevated temperatures [13]. ZrC/W composites are also attractive for aerospace applications, as the relatively low density of zirconium carbide can offer a

significant savings in weight relative monolithic tungsten ($\rho[\text{ZrC}] = 6.63 \text{ g/cm}^3$; $\rho[\text{W}] = 19.3 \text{ g/cm}^3$ [6]).

A novel process for fabricating dense, near net-shaped, carbide/refractory metal composites has recently been developed at Ohio State University: the Pressureless Reversible Infiltration of Molten Alloys – Displacive Compensation of Porosity (PRIMA-DCP) method [14-16]. Unlike the conventional processing of ZrC/W composites, which has relied upon high temperature ($\geq 2000^\circ\text{C}$) hot pressing of mixed powders [5,11], the PRIMA-DCP process utilizes relatively low temperatures ($\leq 1300^\circ\text{C}$) and atmospheric pressures. As for the fabrication of W/Cu and W/Ag composites, the PRIMA-DCP process involves the pressureless infiltration of a molten metal into a porous, rigid preform. However, for the PRIMA-DCP process, the metallic liquid contains a reactive element that undergoes a displacement reaction with a ceramic phase (carbide, nitride, boride, oxide, etc.) in the preform. Reactions are chosen such that the total volume of the solid products is greater than the volume of the solid reactant [17]. As a result, the prior pores in the rigid preform become filled with the new solid products, with little change in external shape or dimensions. This increase in internal solid volume also forces residual metallic liquid back out of the composite body ("reversible infiltration"). Dense, near net-shaped composites can be produced; that is, extensive post-reaction machining with diamond tooling can be avoided [14-16]. The objective of the present paper is to demonstrate the feasibility of using the PRIMA-DCP process to produce very high melting, dense, co-continuous W/ZrC-bearing composites with $> 40 \text{ vol\% W}$ at low temperatures ($\leq 1300^\circ\text{C}$).

EXPERIMENTAL PROCEDURE

W/ZrC-based composites were produced by the infiltration and reaction of Cu-Zr liquid with porous W_2C preforms. W_2C powder (99.5% purity, -325 mesh, Cerac Inc., Milwaukee, WI) was mixed in a mortar and pestle with 5 wt% of an aqueous 4 wt% solution of polyvinyl alcohol (Grade Airvol 205, Air Products and Chemicals, Inc., Allentown, PA). The preforms were produced in the shape of discs (13 mm diameter X 2.5 mm thick) by uniaxial pressing of the powder/binder mixtures at a peak stress of 300 MPa. The binder was then removed by heating to 400°C for 4 hours in flowing, titanium-gettered Ar. The preforms were then fired in flowing Ar for 4 hours at 1450°C (i.e., to increase the rigidity of the preform by allowing necks to form between W_2C particles).

The porous, rigid W_2C preforms were infiltrated with molten Zr_2Cu ($T_m = 1025^\circ\text{C}$ [18]). A 1 kg ingot of Zr_2Cu was produced by induction melting of a copper rod (2.5 cm dia. x 5.9 cm thick, 99.99% pure, Atomergic Chemetals,

Farmingdale, NY) and zirconium sponge (0.8-19 mm dia. pieces, 99.6% pure, Johnson-Matthey, Inc., Ward Hill, MA) within a magnesia crucible (99.4% pure, 96% dense, Ozark Technical Ceramics, Inc., Webb City, MO). Prior to melting, the Zr-Cu charge was placed within a silica enclosure that was repeatedly evacuated and backfilled with Ar (99.998% pure). Induction melting/stirring was then conducted with a 60 kV power supply for 4 minutes. The melt was allowed to cool to room temperature within the silica vessel under controlled atmosphere. The composition of the ingot was evaluated by inductively coupled plasma spectroscopic analysis (Optima 3000 ICP-OES, Perkin-Elmer Corp., Norwalk, CT).

Prior to a given reactive infiltration experiment, pieces of the solid Zr_2Cu ingot were placed on a porous W_2C preform. The W_2C preform was supported on two 0.9 mm diameter graphite rods, inside a graphite-foil-lined magnesia crucible (Ozark Technical Ceramics). The molar ratio of $Zr_2Cu:W_2C$ used in each experiment was 0.86-0.9:1, which was in excess of the amount required for complete consumption of the W_2C . After purging the tube furnace with dry, flowing, titanium-gettered Ar for 2 hours, the Zr_2Cu -covered preforms were heated at $7^\circ C/minute$ to $1300^\circ C$ and held for 2 hours. The specimens were then cooled at $7^\circ C/minute$ under the flowing argon atmosphere. After extraction from the furnace, the thin layer of excess Cu-Zr metal adhering to the specimen was removed by light sanding with SiC paper.

The phase content and microstructure of the starting reactants (as powders) and resulting composite specimens (as polished cross-sections) were evaluated with x-ray diffraction (XRD) analyses (i.e., using $Cu-K\alpha$ radiation and a scan rate of $1^\circ/minute$) and scanning electron microscopy (SEM, Model XL-30, Philips Electron Instruments, Eindhoven, The Netherlands). Microchemical analyses (EDX) were conducted with a Si/Li detector (EDAX International, Mahwah, NJ) attached to the electron microscope, using at least 3 measurements for each phase. Image analyses (Clemex Vision version 3.0.027 software, Langueuil, Quebec, Canada) of backscattered electron images (≥ 10 for each sample) were also conducted to determine the average phase contents and phase sizes of reacted composites.

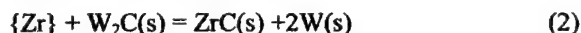
RESULTS AND DISCUSSION

Prior work has shown that dense, near net-shaped, carbide-rich composites can be generated by the following PRIMA-DCP reaction [14-16]:



where {Zr} refers to zirconium dissolved within molten Zr_2Cu . Molten Zr_2Cu was used, instead of pure zirconium, in order to dramatically lower the temperature required for melting and infiltration (i.e., the melting point of Zr_2Cu , 1025°C, is about 800°C lower than for pure Zr [18]). This reaction was conducted by allowing molten Zr_2Cu to infiltrate into porous WC preforms at 1200-1300°C and at ambient pressure [14-16]. The total volume of the solid products, ZrC and W, for this reaction is 101% larger than the volume of the solid reactant, WC [6]. Hence, in order to provide sufficient pore space within the rigid preform so as to accommodate this increase in internal solid volume upon completion of reaction (1), a WC preform needs to possess a porosity of ≥ 50.2 vol%. Full conversion of WC preforms with 50.2% porosity should yield composites with 38.0 vol% tungsten. Reactive infiltration of WC preforms with less than 50.2% porosity should result in pore filling prior to complete consumption of the WC; that is, composites with residual WC and, hence, less ZrC and W, should be generated in this case. Indeed, dense, carbide-rich (ZrC + WC) composites with only 20.3 vol% tungsten have been generated from relatively dense WC preforms [14-16]. On the other hand, WC preforms with a higher porosity can be fully converted into ZrC and W prior to complete pore filling. In the latter case, a relatively high amount of excess Cu-rich liquid will remain in the composite.

Composites with relatively high tungsten contents (> 40 vol%) were desired in the present work. The tungsten content of PRIMA-DCP-derived ZrC/W composites may be increased by: i) replacement of WC in the preform with W_2C , ii) adding tungsten metal to the preform, or iii) combinations thereof. The relevant displacement reaction for preforms comprised of W_2C is:



As for reaction (1), this reaction is strongly favored from a thermodynamic perspective [19]. The complete consumption of W_2C by reaction (2) should yield composites comprised of 55.1 vol % tungsten and 44.9 vol% zirconium carbide [6]. The total volume of the solid products for this reaction is 56.5% larger than the volume of the solid reactant, WC [6]. Hence, a rigid W_2C preform needs to possess a porosity of ≥ 36.1 vol% in order to provide sufficient pore space so as to accommodate the increase in internal solid volume upon completion of reaction (2).

X-ray diffraction analysis of the as-received, starting carbide powder is shown in Figure 1a. The powder used to prepare the preforms was comprised of predominantly W_2C along with a small amount of WC. After pressing this powder into disks and firing for 2 hours at 1300°C, the resulting disks possessed

an average bulk density of 10.35 g/cm^3 . If the disk is assumed to consist of only W_2C , this bulk density value corresponds to a porosity of 39.6% [6]. Since the preforms also contained a small amount of WC, the actual porosity value must have been slightly lower than 39.6%. Secondary and backscattered electron images of polished cross-sections of the W_2C -rich disks after reactive infiltration with molten Zr_2Cu for 2 hours at 1300°C are shown in Figures 2a and 2b, respectively. The secondary electron image reveals a dense specimen with only a few fine ($<1 \text{ }\mu\text{m}$ dia.), isolated pores. Three distinct phases were detected within the backscattered electron image: a white particulate phase; a predominant, dark matrix phase; and a second, minor matrix phase with a gray coloration between the two former phases. EDX analyses indicated that the white particulate and dark matrix phases were comprised of tungsten and zirconium carbide, respectively. Although the phase size of the lighter matrix phase was too fine for unambiguous EDX analysis, this phase was found to be enriched in copper. XRD analysis of this reacted specimen (Figure 1b) revealed diffraction peaks for ZrC and W. Distinct diffraction peaks for a Cu-enriched phase were not detected, presumably due to the relatively small amount of this phase in the final composite. The zirconium carbide and tungsten crystallites in the composite of Figure 2 were quite fine. Image analyses indicated that the average ZrC and W phase sizes were $0.66 \pm 0.25 \text{ }\mu\text{m}$ and $0.75 \pm 0.33 \text{ }\mu\text{m}$, respectively. This reaction-formed ZrC/W-bearing composite was found to consist of $45.9 \pm 3.5 \text{ vol\%}$ tungsten, $39.6 \pm 3.7 \text{ vol\%}$ zirconium carbide, and $14.5 \pm 2.3 \text{ vol\%}$ of the copper-rich phase (i.e., a volumetric tungsten to zirconium carbide ratio of 1.16:1).

The presence of some excess, residual Cu-rich metal in the final composite resulted from excess porosity in the preform; that is, the preform possessed a slightly higher porosity than was required (i.e., about 39.6% vs. 36.1%) to accommodate the volume change upon conversion of the preform into zirconium carbide and tungsten. Hence, not all of the Cu-rich liquid could be squeezed out of the specimen upon complete consumption of the W_2C . The tungsten content of the final composite was lower than was predicted for full conversion of W_2C into ZrC and W by reaction (2) (i.e., $45.9 \pm 3.5 \text{ vol\%}$ vs. 55.1 vol%). This discrepancy can be attributed to two factors: i) the presence of some WC in the starting preform, and ii) the nonstoichiometry of zirconium carbide. As mentioned above, the consumption of WC by reaction (1) results in a composite with a lower W content than for the consumption of W_2C by reaction (2). It is well known that zirconium carbide can exhibit appreciable carbon deficiency relative to the stoichiometric ratio $\text{Zr:C} = 1:1$ [20]. Indeed, recent work on the PRIMA-DCP process has revealed that a carbon-deficient composition, $\text{ZrC}_{0.676}$,

is generated via reaction (1) at 1300°C [14]. Reaction (2) can be re-written as follows to take such nonstoichiometry into account:



Complete consumption of W_2C by this reaction should yield composites comprised of 45.3 vol% tungsten and 54.7 vol% zirconium carbide (note: the molar volume of $\text{ZrC}_{0.676}$ was obtained from reference [20]). This reduced tungsten content relative to reaction (2) was not far from the observed value (45.9 ± 3.5 vol%) for the composite shown in Figure 2

CONCLUSIONS

The feasibility of fabricating dense, carbide-bearing composites with substantial refractory metal content at a modest temperature by the PRIMA-DCP process has been demonstrated. Dense ZrC/W-bearing composites with 45.9 vol% W were produced by the infiltration (pressureless) and reaction of molten Zr_2Cu with a porous W_2C -bearing preform at 1300°C (note: this processing temperature was far below the melting points of zirconium carbide and tungsten). The tungsten and zirconium carbide phases in the dense composites were found to be quite fine. The final phase content was consistent with the starting preform porosity, the reaction-induced change in internal solid volume, and the nonstoichiometry of zirconium carbide.

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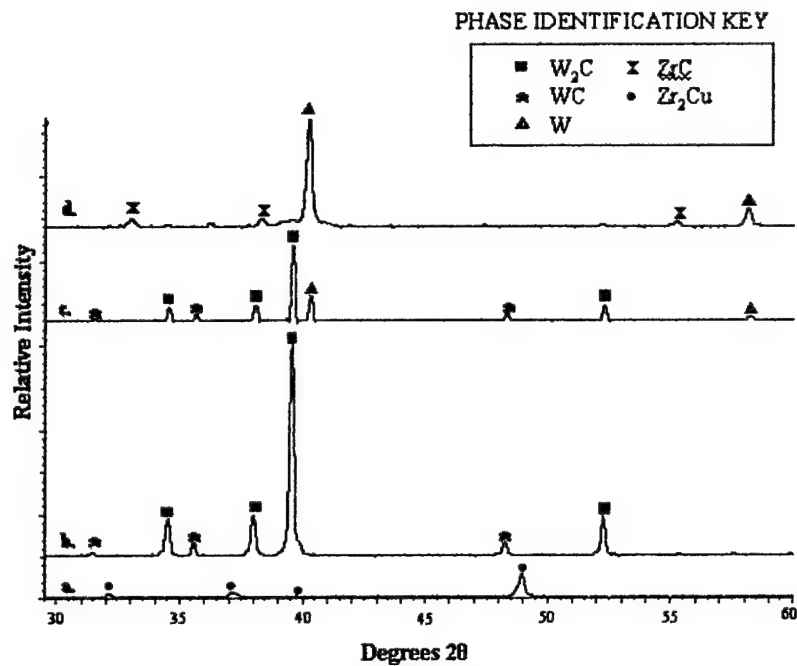


Figure 1: X-ray diffraction pattern of **a.** Zr_2Cu powder. **b.** Received W_2C powder. **c.** Lightly sintered W_2C preform body. **d.** W/ZrC composite formed by the reaction of An oxidized W_2C preform (see **c**) with Zr_2Cu (l) at $1300^\circ C$ for 8 hours. All major peaks represented within shown angular range ($30-60^\circ 2\theta$).

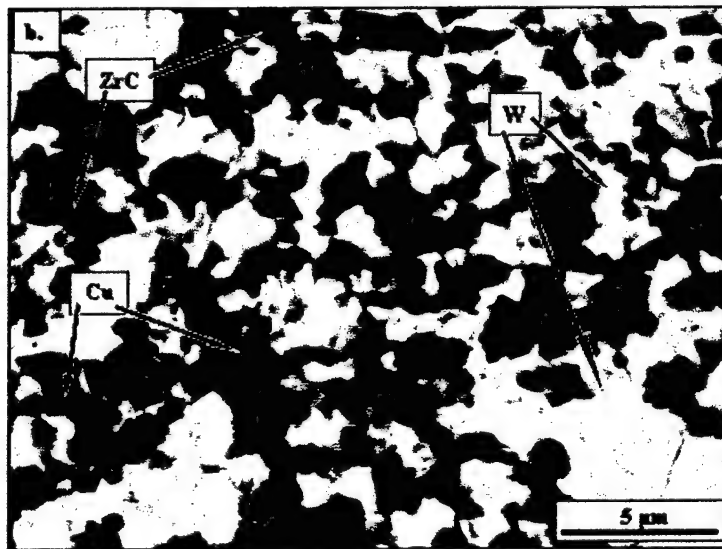
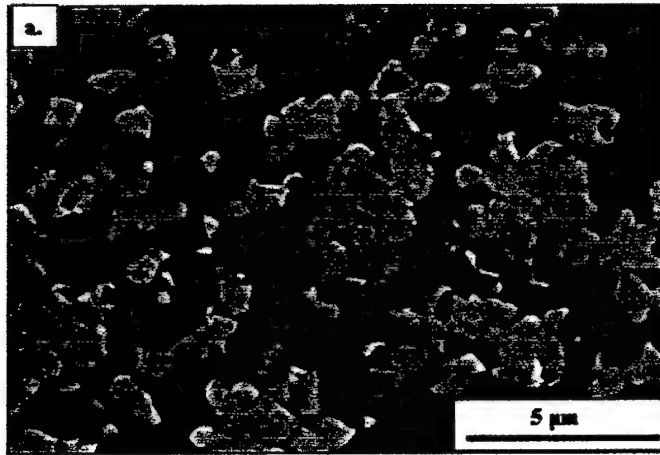


Figure 2: a.) Secondary and b.) backscattered electron image of a polished cross-section of a W/ZrC composite produced by the PRIMA-DCP process (reactive infiltration of $\text{CuZr}_2(\text{l})$ into porous $\text{W}_2\text{C}(\text{s})$ at 1300°C for 2 hours) with phases identified.

Near net-shape, ultra-high melting, recession-resistant rocket nozzles: I. Fabrication of ZrC/W-based nozzle inserts via the displacive compensation of porosity (DCP) method

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Abstract

Ultra-high-melting carbide/refractory metal composites can exhibit an attractive combination of thermal, chemical, and mechanical properties for high temperature aerospace applications (e.g., rocket nozzles, leading edges, combustion chambers, exhaust flaps). Dense, near net-shaped ZrC/W-based composites have been fabricated at modest temperatures and at ambient pressure by a recently-patented reactive (pressureless) infiltration process known as the Displacive Compensation of Porosity (DCP) method. Porous WC preforms with hourglass shapes (for rocket nozzle liners) were produced by gel casting, whereas simple bar-shaped preforms were produced by uniaxial pressing. The porous preforms were exposed to molten Zr_2Cu at 1200-1300°C and ambient pressure. The Zr_2Cu liquid rapidly infiltrated into the preforms and underwent a displacement reaction with the WC to yield a more voluminous mixture of solid products, ZrC and W. This displacement reaction-induced increase in internal solid volume filled the prior pore spaces of the preforms ("displacive compensation of porosity") to yield dense, ZrC/W-based composites. Because the preforms remained rigid during reactive infiltration, the final composites retained the external shapes and dimensions of the starting preforms. The DCP process enables dense, ceramic/refractory metal composites to be fabricated in complex and near net shapes at modest temperatures without the need for high-pressure densification or extensive machining.

Key Words: zirconium carbide, tungsten, ceramic/metal composites, gel casting, reactive infiltration, displacive compensation of porosity, displacement reaction, oxidation-reduction, near net shape, rocket nozzles

1. Introduction

The ever more demanding requirements for enhanced performance in aerospace vehicles continue to provide new opportunities for advanced materials. Novel, high-melting, lightweight materials that are chemically, mechanically, and thermally robust are needed to allow for significant improvements in the operating conditions and lifetimes of key rocket and jet engine components (e.g., nozzles, valves, combustion liners, exhaust flaps, leading edges) [1,2]. Among the most severe environments encountered in aerospace applications exists in the throat region of a solid-fueled rocket nozzle. Solid, aluminum-bearing fuels generate combustion products (molten aluminum oxide droplets and gas) that impact the nozzles at supersonic speeds and at temperatures in excess of 2500°C [3-5]. Under these extreme conditions, rocket nozzle materials need to exhibit minimal vaporization, erosion, ablation, and creep [1-7]. Nozzle materials must also be highly resistant to thermal shock, given the rapid rise in temperature upon ignition [1,2,4,5,8]. Among the refractory metallic materials, tungsten possesses the highest melting point (3422°C) and is relatively noble (minimal volatilization and oxidation) under the extreme temperatures and reaction conditions within solid, aluminum-fueled rocket nozzles [9-12]. However, the high density (19.3 g/cm³), reduction in strength at elevated temperatures, and fabrication costs for monolithic tungsten make this material less than ideal for rocket components [10-16].

Composites of refractory metals with covalently-bonded ceramics can possess attractive properties for high-temperature rocket applications. Consider, for example, composites of tungsten and zirconium carbide. Zirconium carbide is a hard (up to 2900 kg/mm²), high melting (up to 3540°C) compound that is considerably lighter than tungsten (the density of ZrC, 6.63 g/cm³, is about one-third of the density of W) [13,17,18]. Tungsten and zirconium carbide are

chemically, thermally, and mechanically compatible. These phases exhibit little mutual solid solubility at elevated temperatures (e.g., ≤ 7 mol% at 2800°C) and do not react to form other compounds [19]. Unlike many ceramic/metal composite systems, zirconium carbide and tungsten possess similar thermal expansion coefficients (e.g., $4.5 \times 10^{-6}/^{\circ}\text{C}$ for W vs. $4.0 \times 10^{-6}/^{\circ}\text{C}$ for ZrC at room temperature; $9.2 \times 10^{-6}/^{\circ}\text{C}$ for W vs. $10.2 \times 10^{-6}/^{\circ}\text{C}$ for ZrC at 2700°C) [20,21]. Both phases also possess relatively high thermal conductivities (105 ± 10 W/m-K for W, and 40 ± 10 W/m-K for ZrC over the temperature range of 1000-2200°C) [22,23]. As expected from these thermal properties, ZrC/W composites have been found to be resistant to thermal shock [24]. The carbide phase should endow co-continuous ZrC/W composites with enhanced high-temperature stiffness and creep resistance relative to monolithic tungsten, whereas the ductility of tungsten above 400°C (i.e., above the brittle-to-ductile transformation temperature) should provide enhanced resistance to fracture relative to monolithic zirconium carbide [10,11,14-16,18]. Indeed, Song, et al. have reported that a W/ZrC composite with 30 vol% ZrC possessed enhanced stiffness relative to monolithic tungsten at 1200°C (about 345 GPa for W/ZrC vs. about 270 GPa for W) [25]. Such composites also exhibited flexural strengths (three-point bending) of 810 MPa at 1200°C [25].

Although dense ZrC/W composites have been produced by high-temperature hot pressing (e.g., at 2000°C and 20 MPa [24-26]), this process is relatively slow and expensive, and is not well-suited for the fabrication of complex-shaped composites such as rocket nozzles. An attractive alternative method for fabricating dense carbide/refractory metal composites in complex shapes is the recently-patented Displacive Compensation of Porosity (DCP) method [27-35]. With the DCP process, a shaped, porous ceramic preform is infiltrated at ambient pressure with a low-melting, reactive metallic liquid. Upon infiltration, the liquid undergoes a

displacement reaction with the ceramic preform to generate new ceramic and metal phases within the preform. Unlike other reactive infiltration methods, reactions are chosen that yield a ceramic product with a larger molar volume than the ceramic reactant [27,28]. Hence, as the displacement reaction proceeds within the infiltrated preform, the prior pore volume becomes filled with new solid ("displacive compensation of porosity"). The excess metallic liquid is then gradually squeezed back out into the surrounding liquid bath, so that a dense, ceramic-rich composite is produced. If the porous preform is lightly sintered prior to infiltration, so that the ceramic particles in the preform are necked, then the preform remains rigid as the internal network of reactant ceramic is replaced by the more voluminous solid product(s). The process is completed when either the ceramic reactant is fully consumed or the pores become filled with solid material, whichever happens first (in the latter case, the kinetics of reaction slow appreciably prior to complete consumption of the reactant ceramic phase). The final dense composite retains the shape and dimensions of the starting rigid preform (i.e., near net-shape processing). By using thermodynamically-favored internal reactions at modest temperatures to generate desired high-temperature phases and to fill porosity, the DCP process avoids the need for densification by high-pressure or high-temperature sintering. Furthermore, low-cost conventional ceramic processes (e.g., slip casting, gel casting, powder injection molding, etc.) may be used to produce porous ceramic preforms with complex shapes that are then preserved upon DCP conversion. That is, extensive, time-consuming, and costly diamond machining of green or sintered ceramic bodies is not required to obtain complex shapes. To date, the DCP process has been used to fabricate a variety of dense, near net-shaped ceramic/metal composites (e.g., MgO/Mg-Al, $\text{MgAl}_2\text{O}_4/\text{Fe-Ni-Al}$, MgO/FeAl, ZrC/W) at modest temperatures [27-35]. However, such prior work involved the fabrication of dense composites with relatively simple

shapes (disks, bars, plates). The goal of this paper is to demonstrate that the DCP method can be used to fabricate complex-shaped, ZrC/W-based rocket nozzle inserts. The performance of such nozzles in a solid-fueled rocket test is discussed in the companion paper (Part II).

2. Experimental procedure

Composites of zirconium carbide and tungsten were generated by the reactive infiltration of $\text{Zr}_2\text{Cu(l)}$ into porous tungsten carbide preforms. WC preforms in the shape of an hourglass (for rocket nozzle inserts) were prepared by gel casting. A mixture of 43 vol% WC powder (99.9% purity, 5.6 μm ave. size, Novel Technologies, Inc., Morristown, TN) with an aqueous solution containing 6.4 wt% of a proprietary gelling agent (MetaMateria Partners, LLC, Columbus, OH) was cast into an aluminum mold. After allowing the casting to set for 45 min, the mold was removed and the casting was allowed to dry at room temperature and then overnight at 55°C. The casting was then heated in flowing Ar to 400°C for 4 h (to remove the organic material) and then to 1450°C for 4 h (to produce rigid preforms). WC preforms in the shapes of bars were also prepared by uniaxial pressing of a mixture of the WC powder with 5 wt% of an aqueous solution of 4 wt% polyvinyl alcohol (Airvol 2005 PVA, Air Products and Chemicals, Allentown, PA). The mixture was uniaxially pressed into bars (11 mm long X 9.9 mm wide X 2.5 mm thick) at a peak stress of 300-340 MPa. The green bars were heated to 400°C for 4 h in flowing Ar (to remove the PVA binder) and then to 1600-1700°C for up to 2 h in a vacuum furnace (to produce rigid preforms).

Zr_2Cu ingots were prepared by induction melting or by arc melting. For induction melting, a 1 kg charge comprised of zirconium sponge (99.6% purity, 0.8-19 mm dia. pieces, Johnson-Matthey, Ward Hill, MA) and a copper rod (99.99% purity, 2.5 cm dia. X 5.9 cm thick,

Atomergic Chemetals, Farmingdale, NY) was placed within a magnesia crucible (96% dense, 10.2 cm dia. X 15.2 cm high, Ozark Technical Ceramics, Webb City, MO). The charge was then sealed within a silica enclosure located inside a water-cooled copper coil connected to a 60 kV induction power supply (Mark IV, Inductotherm, Rancocas, NJ). After repeated evacuation and backfilling with argon, the charge was induction melted and stirred for 4 minutes. Inductively-coupled plasma spectroscopy (Optima 3000 ICP-OES, Perkin Elmer Corp., Norwalk, CT) indicated that the solidified ingot possessed a composition of 67.5 at% Zr/32.5 at% Cu, which was close to the desired Zr_2Cu composition. X-ray diffraction (XRD) analyses of the ground ingot also revealed peaks consistent with Zr_2Cu . Arc melted Zr_2Cu ingots were prepared by ACI Alloys, Inc. (San Jose, CA). Charges of 0.6 kg comprised of a mixture of zirconium chips (99.8 wt% purity, 1 cm X 1 cm X 0.1 mm thick) and copper cylinders (99.99 wt% purity, 6 mm dia. X 4 cm long) were melted with a single arc on a water-cooled copper hearth into disk-shaped ingots (8-10 cm dia. X 1.3 cm thick). To allow for homogenization, each ingot was flipped and remelted at least once, with a total exposure time to the arc of at least 15 min. XRD analyses of the solidified arc-melted ingots yielded peaks consistent with Zr_2Cu .

Reactive infiltration of the nozzle-shaped WC preforms was conducted by immersion in a $\text{Zr}_2\text{Cu(l)}$ bath. Prior to immersion, the nozzle-shaped preform was suspended above the bath on a graphite support. The $\text{Zr}_2\text{Cu(l)}$ bath was contained within a cylindrical magnesia crucible (96% dense, 15.2 cm dia. X 15.2 cm tall, Ozark Technical Ceramics). The molar ratio of Zr_2Cu in the bath to WC in the preform was 8.8:1, which was well in excess of the amount required for complete consumption of the WC. After thermal equilibration of the preform and the bath at 1200°C in a 3% H_2/Ar flowing gas atmosphere, the preform was lowered into the $\text{Zr}_2\text{Cu(l)}$ bath. After immersion for 10 minutes, the preform was raised above the bath and heated at 2°C/min to

1300°C. The preform was then cooled to room temperature. For the smaller bar-shaped WC preforms, pieces of the solid Zr₂Cu ingot were placed on top of the WC plates within a flat-bottomed magnesia combustion boat (96% dense, 1.27 cm deep X 10.2 cm long X 5.1 cm wide, Ozark Technical Ceramics). The molar ratio of Zr₂Cu:WC used in the bar infiltration experiments was maintained at 1.5-1.6:1, (i.e., in excess of the amount required for complete consumption of the WC). The Zr₂Cu-covered preforms were heated at 7°C/min to 1200-1300°C for 1-8 h and then cooled at 7°C/min to room temperature. The phase content and microstructure of the resulting composites were evaluated with a scanning electron microscope (XL-30 SEM, Philips Electron Instruments, Eindhoven, The Netherlands) equipped with an energy-dispersive x-ray (EDX) detector (Edax International, Mahwah, NJ) and with XRD analyses.

3. Results and discussion

3.1 The liquid/solid displacement reaction

The following type of liquid/solid displacement reaction was used to convert porous WC preforms into dense ZrC/W-based composites:



where {Zr} refers to zirconium dissolved within a molten metallic solution. This reaction is strongly favored from a thermodynamic perspective and is of the DCP type; that is, the sum of the molar volumes of the solid products, ZrC and W, is twice the molar volume of WC (i.e., $V_m[ZrC] + V_m[W] = 2.01V_m[WC]$) [13,36]. An alloyed Zr-bearing melt was used in this reaction to reduce the temperature required for melting and infiltration processing (i.e., to avoid the energy costs and complications associated with handling pure zirconium liquid, which melts at 1855°C [37]). Copper was selected as the alloying element for the zirconium-bearing liquid in

this work. Several congruently-melting compounds exist in the Zr-Cu system with melting points below 1150°C (note: congruently-melting Zr-Cu compounds were preferred, in order to avoid phase separation and uncontrolled segregation during melt infiltration) [37]. The most zirconium-rich of these Zr-Cu compounds, Zr_2Cu , was selected as the melt composition for the present work. Although comprised of two-thirds zirconium, the melting point of Zr_2Cu (1025°C) is more than 800°C below that of pure zirconium [37]. Other important considerations in selecting an alloying element for the Zr-bearing melt were: i) the reactivity of the element with ZrC and with W, and ii) the influence of such an element on the performance of ZrC/W-based composites in the rocket nozzle environment. The latter criterion can be important, even in the absence of appreciable reaction of the alloying element with W or ZrC, due to the inevitable entrapment of a small amount of this element in the final composite during the DCP process. Copper exhibits minimal chemical reaction with tungsten; that is, stable compounds do not form between Cu and W at ambient pressures, and the solidus temperature of tungsten is only slightly reduced in the presence of copper (from 3422 to 3414°C) [9]. Copper also does not react with zirconium carbide to form a more stable carbide [36,38]. Small amounts of retained copper in a ZrC/W-based composite may enhance the performance of such composites. Indeed, the addition of copper as a secondary phase has been used for enhanced transpirational cooling of tungsten-based, solid-fueled rocket nozzles (i.e., the latent heats of fusion and of vaporization of copper can be used to absorb some of the heat experienced by a solid-fueled rocket nozzle) [12,39]. Modest additions of copper may also enhance the ductility and toughness (particularly at room temperature) along with the thermal conductivity of the ZrC/W-based composites [40].

3.2 Phase and microstructural characterization of DCP-derived composites

Secondary and backscattered electron images of polished cross-sections of a composite generated by the reactive infiltration of $Zr_2Cu(l)$ into a bar-shaped WC preform at $1300^\circ C$ are shown in Figures 1a and 1b, respectively. The WC preform associated with this composite possessed a porosity of 43.5% prior to reactive infiltration. The secondary electron image in Figure 1a revealed that, after reactive infiltration, the specimen was comprised of a particulate phase encased within a dense matrix. Only a few isolated, fine ($< 2 \mu m$) pores were detected within the matrix or particulate phases. The higher-magnification backscattered electron image in Figure 1b revealed that the particles consisted of a grey core and a relatively bright coating. The coated particles were enveloped by a darker matrix phase. The matrix phase was found to be enriched in zirconium and carbon by EDX analyses, which was consistent with zirconium carbide. EDX analyses revealed that the grey core of the particles was comprised of tungsten and carbon, whereas the bright coating was enriched in tungsten (depleted in carbon). These EDX analyses, coupled with the differences in phase contrast observed in the backscattered electron image, were consistent with residual (unreacted) tungsten carbide particles coated with a tungsten layer. The composite associated with the images in Figures 1a and 1b was generated by exposure to $Zr_2Cu(l)$ for 8 h. Composites with similar microstructures were also produced after only 0.5 h of exposure of WC preforms of comparable porosity (42.4 vol%) to the Zr_2Cu melt (Figure 1c). XRD patterns obtained after exposure of WC preforms (with porosities of $46 \pm 1\%$) to the Zr_2Cu melt at $1300^\circ C$ for various times are shown in Figure 1d. Similar amounts of ZrC, W, and WC were detected for reaction times of 0.5 to 8 h [13]. Weak diffraction peaks consistent with copper were also observed. Small, isolated amounts of a Cu-rich phase (not seen

in Figures 1a-c) were also occasionally detected by EDX analyses in polished composite cross-sections.

The ZrC matrices and the W coatings on particles observed in the microstructures in Figures 1a-c were generated within the pore spaces present in the starting WC preforms. The presence of residual WC in these reacted specimens was a result of pore filling prior to complete consumption of the WC. The WC preforms used to generate the composites shown in Figures 1a-1c possessed porosities of 42.4-47.0 vol%. These values of porosity were smaller than what was required to accommodate the internal increase in solid volume from complete conversion of tungsten carbide into zirconium carbide and tungsten (note: in order to accommodate the 101% increase in internal solid volume due to completion of reaction (1), a target porosity of 50.2 vol% was required [13]). Once the pores become filled, further migration of $Zr_2Cu(l)$ into the preform, and further consumption of WC, were inhibited. The similarities in XRD patterns and microstructures of the specimens generated within 0.5 h and 8 h of exposure to $Zr_2Cu(l)$ indicated that the pores were filled, and the reaction was effectively terminated, within 0.5 h at 1300°C.

Secondary electron and backscattered electron images of a polished cross-section of a composite specimen generated by reactive infiltration of $Zr_2Cu(l)$ into a 52.0% porous WC preform are shown in Figures 2a and 2b, respectively. The secondary and backscattered electron images again reveal a dense specimen, containing a few fine ($<2\ \mu m$) isolated pores, comprised of a particulate phase contained within a darker matrix. X-ray maps for carbon, zirconium, and tungsten associated with the backscattered electron image in Figure 2b are shown in Figures 2c, 2d, and 2e, respectively. The matrix phase was enriched in carbon and zirconium, which was consistent with zirconium carbide. The particulate phase was enriched in tungsten and depleted

in carbon, which was consistent with metallic tungsten; that is, the particles did not contain residual tungsten carbide. The uniformity in brightness of the particles in the backscattered electron image (i.e., the absence of a relatively bright cladding layer surrounding each particle), and the presence of distinct scratches through the particulate phase (Figure 2a), were also consistent with particles of relatively soft metallic tungsten in a much harder zirconium carbide matrix. A minor amount of a copper-rich phase was also detected by EDX analyses (Figure 2a). Although small in amount, more of this copper-rich phase was detected in the microstructure of this composite specimen than for composites generated from denser WC preforms. The enhanced porosity (52.0 vol%) of the starting rigid WC preform for this specimen provided sufficient open volume to enable the formation of ZrC and W to be completed (i.e., for the WC to be fully consumed) just prior to complete filling of the pores. The presence of a small, but noticeably larger, amount of a copper-rich phase could be attributed to the slight excess in pore volume beyond that required for complete reaction (i.e., 52.0% porosity in the WC preform vs. the 50.2 vol% required to accommodate the reaction-induced increase in solid volume).

3.3 Near net-shape fabrication of ZrC/W-based rocket nozzle liners

An optical photograph of a porous, nozzle-shaped WC preform prepared by gel casting followed by a modest sintering treatment (1450°C, 4 h) is shown in Figure 3a. The geometry of this preform was chosen to be compatible with the rocket test discussed in the following companion paper (Part II). The bulk density of this preform after light sintering was 7.52 g/cm³, which corresponded to a porosity of 52.0 vol% (i.e., sufficient for completion of reaction (1)). An optical image of the nozzle insert after reactive infiltration with Zr₂Cu(l) is shown in Figure 3b. The same specimen is shown in Figures 3c and 3d after excess solidified metal adhering to the

nozzle surfaces was selectively removed by light polishing (note: the solidified Zr-Cu metal was much softer than the underlying carbide-bearing composite). The weight gain of this nozzle after reactive infiltration was 49.0%, which was not far from that expected (46.6%) for complete conversion of WC into ZrC and W. The nozzle insert retained the shape of the starting porous WC preform. Indeed, the diameters of the entry and exit cones of the nozzle insert changed by ≤ 0.3 mm after reactive infiltration (the ID of the entry cone changed from 9.63 to 9.65 cm; the ID of the exit cone changed from 3.02 to 3.05 cm).

The present work demonstrates the feasibility of using the DCP method to fabricate a complex, near net-shaped, dense composite containing ultra-high-melting non-oxide ceramic and refractory metal phases at ambient pressure and at a temperature far below the ultimate use temperature in solid-fueled rocket nozzles ($>2500^{\circ}\text{C}$). The DCP process is not limited to ZrC/W-based composites. Complex-shaped composites containing a variety of other ceramic phases (carbides, borides, nitrides, oxides, etc.) and refractory metals may also be produced for use in a wide range of high-temperature aerospace (rocket nozzles, combustion liners, leading edges, exhaust flaps, etc.) and other applications (e.g., erosion-resistant dies for extrusion, drawing, pressing or forming; wear-resistant plates for brakes, skids, or runners; stiff, creep-resistant structural components; hard, lightweight armor).

4. Conclusions

Near net-shaped composites containing the ultra-high-melting phases, zirconium carbide and tungsten, were fabricated at modest temperatures and at ambient pressure by the Displacive Compensation of Porosity (DCP) method. Porous, gel-cast WC preforms in the shape of an hourglass (for rocket nozzle liners) were infiltrated at only $1200\text{--}1300^{\circ}\text{C}$ with molten Zr_2Cu .

The zirconium in the liquid displaced the carbon from tungsten carbide to form zirconium carbide and metallic tungsten. Because these latter solid products (ZrC, W) possessed twice the volume of tungsten carbide, the prior pores within the preform became filled by these solid products ("displacive compensation of porosity") and excess liquid was squeezed back out of the preform. Since the WC preform remained rigid during the course of reaction, the external shape and dimensions of the starting preform were preserved in the final nozzle-shaped composite. This work demonstrates that the DCP process may be used to fabricate dense ceramic/refractory metal composites in complex and near net shapes without the need for high pressure or high temperature densification or extensive machining.

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Figure Captions

1. a) Secondary electron and b), c) backscattered electron images of composite specimens generated by the reactive infiltration of $Zr_2Cu(l)$ into porous WC preforms at $1300^{\circ}C$. The specimen in a) and b) was generated from a WC preform (43.5 vol% porosity) after exposure to $Zr_2Cu(l)$ for 8 h. The specimen in c) was produced from a WC preform (42.4 vol% porosity) after exposure to $Zr_2Cu(l)$ for 0.5 h. d) XRD patterns obtained from WC preforms ($46 \pm 1\%$ porosity) after infiltration and reaction with $Zr_2Cu(l)$ for 0.5 h, 2 h, 4 h, and 8 h.
2. a) Secondary electron and b) backscattered electron images of composite specimens fabricated by the reactive infiltration of $Zr_2Cu(l)$ into porous WC preforms (52.0 vol% porosity) at $1300^{\circ}C$. c) C, d) Zr, and e) W x-ray maps associated with the backscattered electron image in b).
3. Optical photographs of: a) a nozzle-shaped WC preform (52.0 vol% porosity), and b) the same specimen after reactive infiltration with $Zr_2Cu(l)$ (immersion for 10 min at $1200^{\circ}C$, followed by heating at $2^{\circ}C/min$ to $1300^{\circ}C$), and c), d) after removal of the excess solidified metal on the nozzle surfaces by polishing.

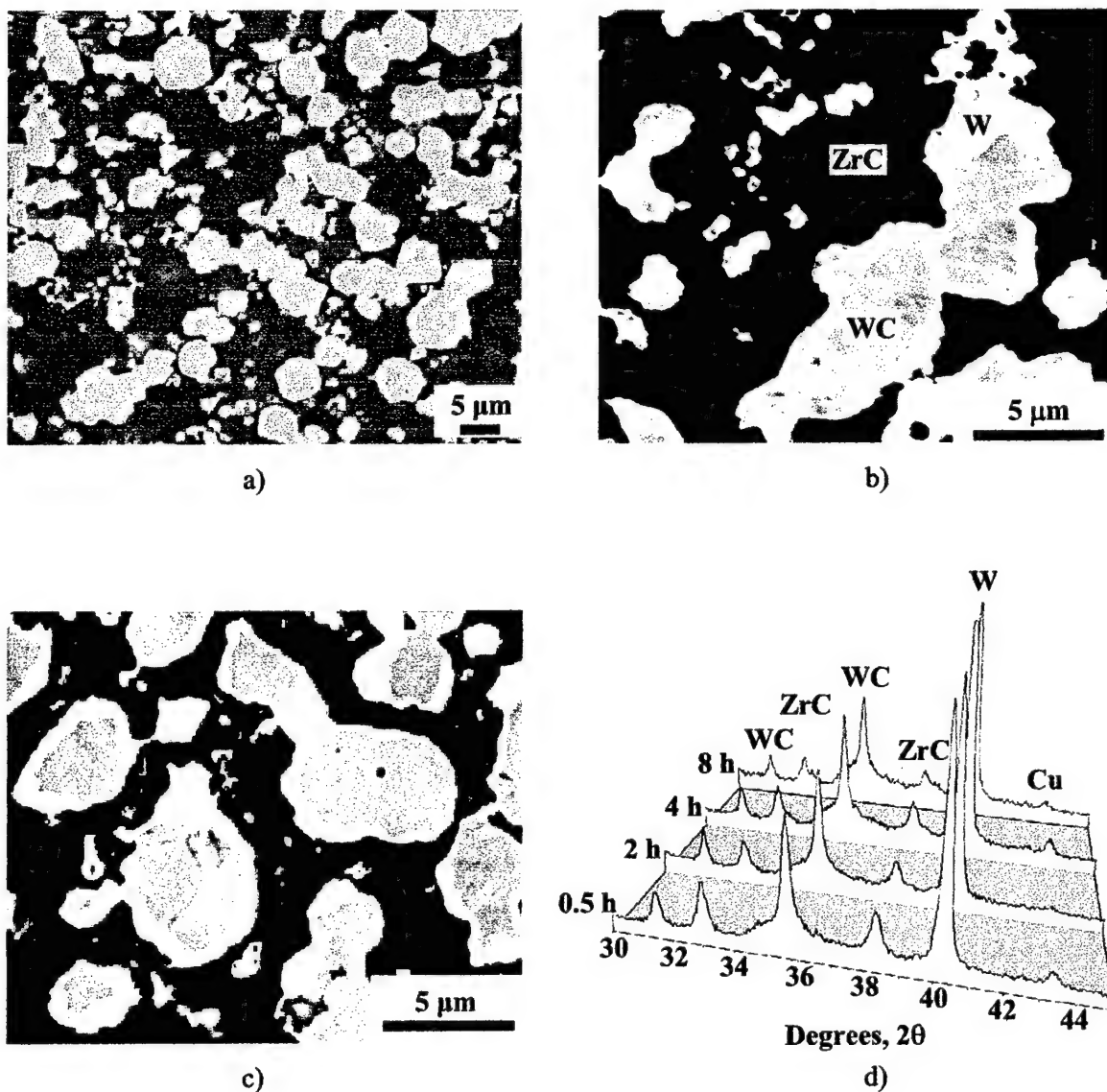
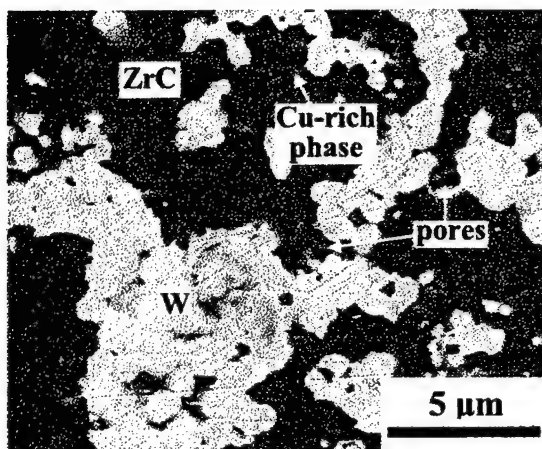
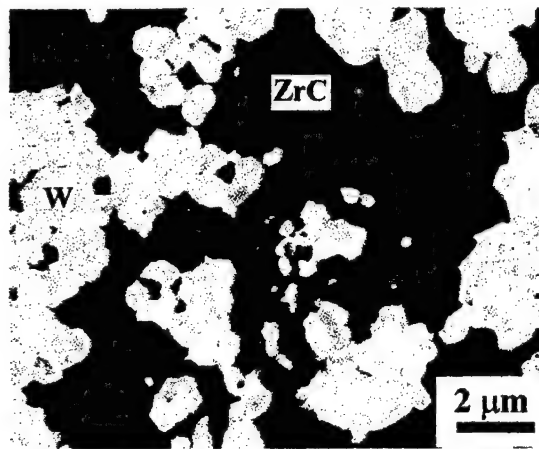


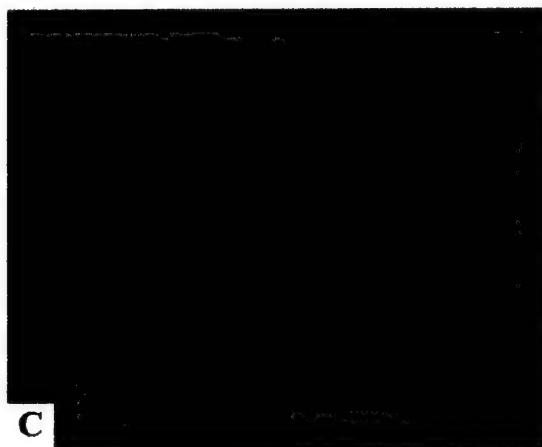
Figure 1. a) Secondary electron and b), c) backscattered electron images of composite specimens generated by the reactive infiltration of $\text{Zr}_2\text{Cu(l)}$ into porous WC preforms at 1300°C . The specimen in a) and b) was generated from a WC preform (43.5 vol% porosity) after exposure to $\text{Zr}_2\text{Cu(l)}$ for 8 h. The specimen in c) was produced from a WC preform (42.4 vol% porosity) after exposure to $\text{Zr}_2\text{Cu(l)}$ for 0.5 h. d) XRD patterns obtained from WC preforms ($46\pm 1\%$ porosity) after infiltration and reaction with $\text{Zr}_2\text{Cu(l)}$ for 0.5 h, 2 h, 4 h, and 8 h.



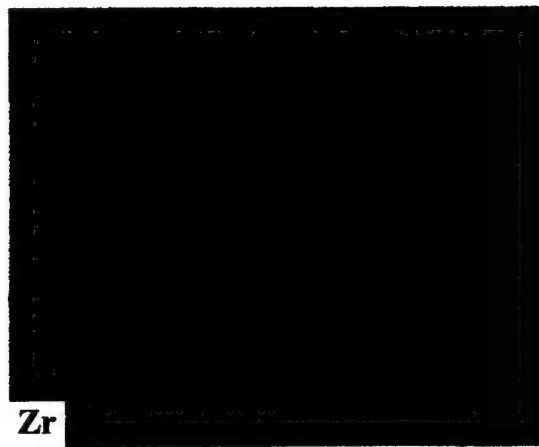
a)



b)



c)

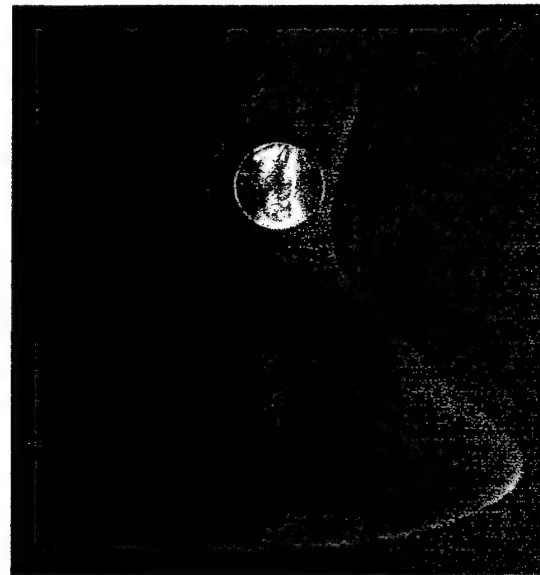


d)



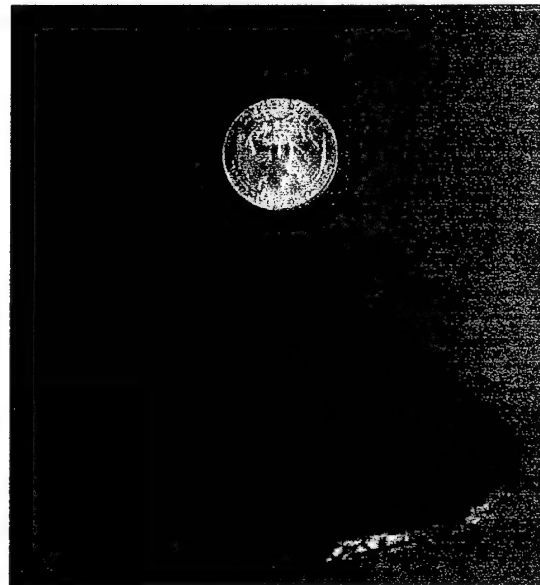
e)

Figure 2. a) Secondary electron and b) backscattered electron images of composite specimens fabricated by the reactive infiltration of $Zr_2Cu(l)$ into porous WC preforms (52.0 vol% porosity) at 1300°C. c), d), e) C, Zr, and W x-ray maps associated with the backscattered electron image in b).



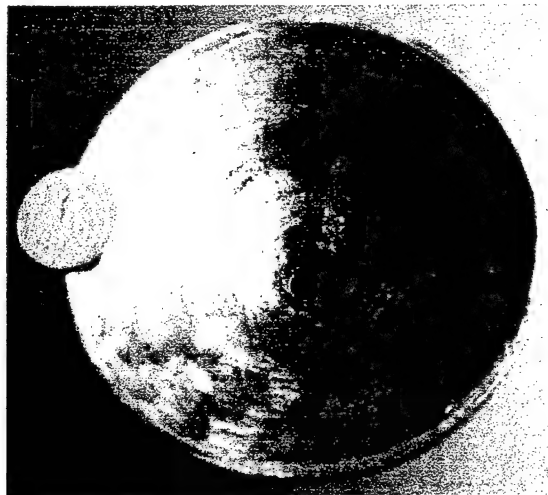
a)

5 cm



b)

Figure 3. Optical photographs of: a) a nozzle-shaped WC preform (52.0 vol% porosity), and b) the same specimen after reactive infiltration with $\text{Zr}_2\text{Cu(l)}$ (immersion for 10 min at 1200°C , followed by heating at 2°C/min to 1300°C), and c), d) after removal of the excess solidified metal on the nozzle surfaces by polishing.



c)



d)

Figure 3 (continued).

Near Net-Shape, Ultra-High Melting, Recession-Resistant Rocket Nozzles II: Low Cost Carbon-

Carbon Technology for use in Ultra-High Temperature Oxidative Environments

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Carbon-carbon composites are ideal materials for high temperature structural uses, such as in rocket propulsion components, hypersonic vehicles, and aircraft brakes. In spite of their excellent properties, the use of carbon-carbon composites has been limited because of their high cost and rapid oxidation at elevated temperatures. Two novel approaches to solving these problems are described and these approaches are employed along with a ZrC/W-based nozzle insert to fabricate and test a recession-resistant carbon-carbon rocket nozzle as a potential replacement for solid tungsten nozzles.

1. Introduction

Carbon-carbon (C-C) composites, which consist of carbon fibers in a carbon matrix, [1-2] possess a unique set of properties that make them ideal materials for high temperature structural uses, such as in rocket propulsion components, hypersonic vehicles, and aircraft brakes. These composites are stronger and stiffer than steel, while less dense than aluminum. In addition, they not only maintain their mechanical properties to temperatures in excess of 3000° C, but the composites' material properties actually improve with heating as the non-ordered carbon is graphitized. In spite of their excellent properties, the use of carbon-carbon composites has been limited because of their high cost and rapid oxidation at elevated temperatures. Extensive efforts over the last 30 years have been unable to resolve these two issues. Now, however, new technical approaches to deal with these two issues have been developed. These approaches will be addressed in this communication along with a demonstration of the technologies developed. The demonstration involves a test firing of a rocket nozzle fabricated utilizing a marriage of the carbon-carbon technologies with the displative compensation of porosity (DCP) process [3-4], to produce a much lighter weight replacement for solid tungsten nozzles currently used in operational systems.

1.1 Fabrication of Carbon-Carbon Composites

The high cost of C-C composites is principally due to the costs associated with the amount of time needed to fabricate the composite which involves the forming and densification of the fiber preform. Except in the case of very high performance or high thermal conductivity fibers, the cost of the raw materials is a very small part of the final composite cost. Likewise, in most applications, the cost associated with forming a preform by the placement of the fibers in the orientations desired to carry any structural load is also not the main cost driver. In the fabrication of most of C-C composites, the major cost is due to the densification of the preform in which a hydrocarbon precursor to the carbon matrix material is placed in the voids between the fibers and the fiber

bundles and then thermally converted to a carbon or graphitic matrix. This is a very expensive process that can take up to nine months per part.

Although there are many different hydrocarbon matrix precursors, there are just two major paths for densifying a carbon fiber preform with these precursors. One process involves infiltrating the composite preform with a hydrocarbon gas, such as methane [5] or propylene [6], while the other process involves impregnating the fiber preform with a liquid hydrocarbon such as a petroleum pitch [7], coal tar pitch [8], refined pitch [9-10], mesophase pitch [11-13], or an organic resin such as phenolic [14]. In all cases the densification process is followed by carbonization in which the matrix precursor is pyrolyzed inside the preform converting it to carbon. In most manufacturing processes, the carbonization step is followed by graphitization in which the partially densified preform is heated to temperatures in the range of 2000° C to 2800° C. This heat-treatment not only converts some types of carbon fibers and matrix carbons to a graphitic structure, enhancing both thermal conductivity and mechanical properties [15], but also opens up a crack network [16] that enhances the effectiveness of further densification steps.

There are numerous densification cycles in most carbon-carbon composite fabrication processes that are necessitated by both the char yield of the matrix precursor and the inhomogeneous densification of the composite. That is, since the carbonization process removes non-carbon atoms from the matrix precursor, the char yield, which is defined as the ratio of the amount of carbon remaining to the amount of hydrocarbon matrix precursor, must be less than 100% and is usually between 40% and 85%. In addition, gases formed during the pyrolysis process tend to push some liquid species out of the fiber preform. As a result of these two processes, void space remains in the partially densified preform after each cycle. This residual void space must be densified on subsequent cycles, which means that ultimate composite density is approached asymptotically.

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The inhomogeneous densification of the composite is manifested in two ways. The predominant effect is the density gradient that exists because both gas phase infiltration and conventional liquid phase impregnations preferentially densify the exterior of the preform. A secondary concurrent effect arises from the closing off of small porosity during deposition. In gas phase infiltration, the gradient results when the gaseous precursor impinges on the hot preform surface and pyrolyzes before it can diffuse very far into the preform. There are several approaches to solve this problem of preferential deposition on the exterior of the preform. These included adjusting residence time of the precursor in the fiber preform [17], employing thermal gradients [18-19], or utilizing the forced flow of matrix precursor gas [20]. Despite these various process modifications, uniform gas phase densification is usually limited to composites with the smallest dimension less than 5 cm.

In a similar manner, a densification gradient results from liquid phase impregnation processes because it is difficult to get the liquid impregnant into the central portion of the preform. This has been assumed by the industry for years to be due to the high viscosity of the precursor but will be shown in this work to be due principally to the lack of wettability of the precursor. To solve this problem, the industry has employed solvents to decrease the viscosity and high pressure to force the impregnant into the preform. Even with this costly process, however, a significant gradient still exists unless the part is subjected to more than ten densification cycles, which is usually cost prohibitive.

As a consequence of the density gradient, after the composite is graphitized, all current commercial densification processes require that the outside of the partially densified composite be machined to remove material. This is necessary because the preferential densification of the exterior of the preform blocks the surface pores so that additional densification cannot occur. Because of the shortcomings of current densification processes, the infiltration/impregnation-carbonization-

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graphitization-machining cycle must be repeated up to 10 times depending on the final density required for the application. Since each cycle requires 3-4 weeks, the densification process is very long and costly.

By understanding and addressing the issues associated with the shortcomings of current commercial processing, the In-Situ Densification Process, developed at the Propulsion Directorate of the Air Force Research Laboratory (AFRL) and described below, is able to avoid inhomogeneous densification and reduce the time required from many months to less than two weeks, with an associated dramatic decrease in cost.

1.2 Elevated Temperature Oxidation of Carbon-Carbon Composites

The principle use of carbon-carbon composites has been and continues to be in the realm of high and ultra high temperature applications such as aircraft brakes and furnace elements as well as in leading edges of hypersonic vehicles, rocket nozzles, exit cones and nose tips. At temperatures above 500 °C, carbon oxidizes rapidly and therefore must be protected from oxygen for maximum performance above this temperature. However, in many applications such as rocket nozzles and nose tips, carbon is unprotected and therefore oxidizes. This oxidation in rocket nozzles results in an enlarged throat region, which leads to a subsequent reduction in thrust, range, and payload for systems utilizing carbon-carbon composite throats. This reduction in performance increases as the throat diameter decreases, and therefore is most severe for tactical missile nozzles.

Many C-C components in use are currently unprotected because the oxidation protection of carbon-carbon composites at ultra high temperature (>2400 °C), or over a wide temperature range, has proven to be an impossible problem to solve over the last 25 years. The main impediment is that carbon-carbon has a thermal expansion coefficient of nearly zero. Thus, any coating that is applied to the surface will have a thermal expansion coefficient 3 to 20 times as great. During

thermal cycling and at high temperatures, a lot of stress develops due to the thermal coefficient mismatch between the composite and the coating. This thermal stress causes the coating to crack and spall off.

Numerous approaches have been used over the years to try to solve this problem. These include graded coatings [21], layered coatings [22], as well as impregnations [23] and functionally-graded coatings [21]. Perhaps the best-known approach is that used for the leading wing edges on the Space Shuttle. This is a silicon carbide coating for oxidation protection and a silica over-layer for crack sealing. Thus, when the leading edge heats up, the silica will melt and form a glass to fill the stress cracks in the silicon carbide. This system works well on the Space Shuttle but does not work at lower temperatures or at temperatures higher than 1600 °C. Thus, an oxidation protection coating for carbon does not exist in the temperature regime in which rocket nozzles and nose tips operate.

Because conventional processing involves graphitization temperatures as high as 2400 °C, it is not possible to place an oxidation protection coating on the composite surface before processing is complete because it will not survive intact at these high temperatures. One work-around for this problem is that coatings are placed on the composites after processing. However, the disadvantage of this technique is that it is not possible to maximize the bond between the coating and the surface of the composite. That leaves the less-than-desirable choices of placing a thick coating on the surface, with the risk of having it crack and possibly spall off, or placing a thin coating on the surface, which will not survive in an erosive environment. These problems associated with the oxidation protection of carbon-carbon composites are solved by employing the Inverse Processing approach described below.

2. Unique Approaches to Solve Intractable Problems

The Propulsion Directorate of the Air Force Research Laboratory (AFRL) at Edwards CA has come up with solutions to both the cost and oxidation problems associated with carbon-carbon composites. AFRL's In-Situ Densification Process addresses the issue of the high cost associated with these composites, while the Inverse Process addresses the problem of oxidation.

2.1 In Situ Densification

In Situ Densification is an impregnation process that, in contrast to commercial processes, is able to rapidly densify the composite uniformly because it addresses the conflicting requirements of the impregnant's low viscosity and good wettability on the one hand and the need for a high char yield carbon precursor on the other.

The key to the success of this process is two-fold. First, it was realized that it is not just the viscosity of the impregnant that is important, as had been assumed for 30 years, but also the contact angle of the impregnant on the surface of the preform. Thus, it has been necessary to employ high pressure in commercial processing for many years, mainly because the impregnants do not wet the surface of the preforms. Viscosity is actually a secondary factor. The second insight was that good wettability, low viscosity, and high char yield do not exist in the same molecule. That is, low molecular weight molecules exhibit lower viscosity and better wettability, while high char yield requires much larger molecules.

To produce a high quality carbon matrix these insights were combined with the results of the extensive work in the production of mesophase pitch by Professor Mochida. [24-26]. Mesophase pitch is the liquid crystal precursor to high quality graphite and for carbon matrices has been produced for more than 30 years by the thermal treatment of coal tar or petroleum pitch. Professor Mochida's important contribution was to realize that mesophase pitch can be produced by the polymerization of pure polyaromatic feedstocks, such as naphthalene [27]. Mesophase is

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commercially produced by this process by Mitsubishi Oil [28] and is used principally in the manufacture of carbon fibers [29-30]. Mitshibutsi Oil and others [31] have used this pitch as a matrix precursor for carbon-carbon composites. Although this pitch produces a high quality matrix material with a char yield of $\sim 84\%$, the process still suffers from the many disadvantages mentioned previously for other processes. In addition, this pitch needs to be oxidatively stabilized to keep it from melting at high process temperatures.

The application of Professor Mochida's approach in the In Situ Process is to use the monomer precursor to the mesophase pitch rather than the pitch itself as the impregnant. Thus, a low viscosity material such as naphthalene, which totally wets carbon surfaces, will enter a carbon fiber preform as easily as water enters a sponge. This not only results in a uniform density, but, in addition, there is also no need for machining after densification to open up the surface pores. After the impregnant has filled the preform, in the second step of the process it is polymerized into a carbon matrix precursor that has a high carbon yield, which means that fewer cycles are needed to bring the composite to final density. The carbon matrix precursor is then pyrolyzed to produce a high quality carbon matrix.

Not only does the In Situ Process produce a uniformly densified composite from any type of fiber preform (woven, braided, 1-D to n-D, felt, etc.) but, in contrast to other processes, there does not appear to be a size limitation. That is, preforms with diameters up to 45 cm and lengths to 183 cm have been uniformly densified with a gradient of $\sim 2\%$. In addition, another unique feature of this technology is the ability to join carbon-carbon parts together with a seamless joint that possesses significant mechanical strength compared to the original parts.

Finally, it should be noted that, in contrast to other processes, it is not necessary to graphitize the composites, which results in significant time and energy savings. Even without graphitization, the ablation and erosion performance of the In-Situ material equals that of

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commercial material when exposed to the exhaust of either liquid rocket engines or solid rocket motors. Thus, in most applications, it is not necessary to graphitize the material. However, when this material is exposed to graphitization temperatures in excess of 2200° C, a highly graphitic material with high thermal conductivity results. The significance of this result is that it is possible to use the low-cost liquid phase process to produce a C-C composite with the properties of a composite produced by employing a gas-phase process.

2.2 Inverse Process

Unlike current densification technologies, the In-Situ process is a relatively low temperature process. That is, since the properties of the carbonized preform are so good and the pore structure remains open, there is no need for graphitization, and thus the composite is only exposed to processing temperatures up to 1000° C rather than 2400° C. With this lower processing temperature, an alternative approach to the oxidation protection of carbon-carbon is possible. With In-Situ processing it is possible to construct a thin shell or an insert out of the oxidation protection material, maximize its properties, and then build the carbon-carbon composite around the insert. This approach, so-called inverse processing, has worked flawlessly. Carbon-carbon rocket nozzles fabricated using inverse processing containing both metallic and ceramic inserts have performed exceedingly well.

In practice, the thin free-standing metallic or ceramic insert is fabricated by any one of a number of processes, such as casting, molding, isostatic pressing, plasma spraying, electro-deposition, etc. The properties of the insert are then enhanced using the appropriate process such as sintering, annealing, densification, etc. A compliant layer is placed on the exterior of the insert and then a carbon fiber preform is wound, laid-up, woven or braided around the insert. The fiber

preform is then densified to the appropriate density and subsequently machined to the dimensions required for the rocket motor.

3.0 Experimental

A ZrC/W-based nozzle insert was manufactured by MetaMateria Partners LLC of Columbus OH using the displacive compensation of porosity (DCP) process [4]. The completed insert was delivered to the Propulsion Directorate of the Air Force Research Laboratory at Edwards CA, where it was prepared for firing in the Pi-k demonstration motor. This preparation consisted of wrapping the insert with continuous T-300 carbon fibers, and densifying the fiber preform using the In Situ Densification process [32] with naphthalene as the matrix precursor. The carbon-carbon composite surrounding the insert was then machined to the final shape required by the test motor. A restraining collar, which actually holds the nozzle in the motor, was then bonded to the carbon-carbon composite that surrounded the exit region of the nozzle.

4.0 Results and Discussion

Tungsten is used as a rocket nozzle material in several Air Force and Navy operational systems. Although it performs adequately, it has a very high density (19.3 g/cm^3). Thus, there is a significant payoff to reduce the weight associated with these nozzles, if possible, to also reduce the recession rate of the throat region associated with the harsh environment to which these nozzles are exposed. The combination of the displacive compensation of porosity (DCP) process described elsewhere [3] and the inverse process described above have the potential to drastically reduce the weight of a nozzle that can be used to replace a solid tungsten nozzle.

The material used in this experiment to make a nozzle insert by the DCP process was a composite of zirconium carbide and tungsten. Because ZrC has a significantly lower density than tungsten ($6.63 \text{ vs. } 19.3 \text{ g/cm}^3$), the DCP-derived ZrC/W-based composite has the potential to reduce the weight of a solid tungsten nozzle by 10-57%. For example, the density of a 20 vol% ZrC

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composite is 10.1% lower than that of pure tungsten; the density of a 50 vol% ZrC composite is 40.6% lower than pure tungsten; and the density of an 80 vol% ZrC composite is 56.8% lower than that of pure tungsten

There is the possibility of very significant additional weight reduction if a thin insert of this metallo-ceramic composite material is used in place of a monolithic metallo-ceramic composite nozzle. For example, if a carbon-carbon composite material with a density of ~ 1.60 g/cc is used as a structural backing material to support the insert, the total weight of the nozzle will be only a fraction of that of a nozzle composed entirely of metallo-ceramic composite material. The resulting macro-composite structure composed of two micro-composite materials is tailorable and thus could possess a wide range of properties.

The ZrC/W-based insert (Figure 1) with a throat diameter of 1.10 cm was delivered by MetaMateria Partners LLC of Columbus OH [4] to AFRL, where it was backed with a carbon-carbon composite. The C-C composite that surrounded the insert had two functions in addition to reducing the overall weight of the completed nozzle: (1) to bring the insert to the final external dimensions required for the motor, and (2) to provide mechanical backing to the insert while the interior of the insert was exposed to the high gas pressure during the firing.

The C-C backing was machined (Figure 2) and a retaining ring was bonded to the carbon-carbon backing. The completed nozzle was then placed in a Pi-K test motor (Figure 3), which had been previously loaded with a solid propellant having a 19% aluminum loading. The temperature that the throat experienced upon combustion of this propellant was predicted by thermal-chemical calculations to be 3245 K.

The propellant grain was ignited and burned (Figure 4) for 4.6 seconds with a maximum pressure of 3.6 MPa. The maximum pressure was limited by the grain design and the amount of propellant that was available for the test. During the test, the nozzle performed extremely well, as

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seen in the pressure trace (Figure 5). The nozzle insert survived the critical initial thermal shock of heat-up and gave a very smooth pressure trace until the small perturbation at the end of the trace. This blip in the pressure was due to the formation of axial hairline compression cracks in the entrance of the ZrC/W insert. These cracks resulted from the fact that there was not a sufficient compliant layer thickness between the insert that was expanding as it was heated and the C-C backing that did not change dimension during the firing.

In designing and manufacturing a C-C backing for the insert, one must allow enough space for expansion but not so much that the insert is unsupported or is loose. Previous firings with other much thinner ceramic and metallic inserts did not show these hairline cracks. However, this was the first test with an insert of this composition and thickness. Since this is a new material, a much thicker insert than has been tested previously, and the ultra high temperature thermal expansion behavior was not known in advance, adequate space for expansion was not provided.

Upon post examination of the nozzle insert, it was observed that the throat had remained intact and the dimensions of the throat had not changed, except for some alumina deposition that can be seen on the exit of the insert (Figure 6). In addition, the surface of the ZrC/W looked unaffected by the firing with no roughening or recession observable. The data obtained during the firing and the post analysis indicated that the nozzle insert performed very well. It was also concluded that the insert would have survived a much longer test since the hairline cracks in the entrance did not allow exhaust gases to reach the carbon-carbon backing.

Conclusion

A recession-resistant rocket nozzle that utilized a ZrC/W-based insert that was backed with a low cost carbon-carbon composite was tested in a solid rocket test motor. The ZrC/W- based insert

fabricated using the displacive compensation of porosity method performed very well with no apparent recession.

Acknowledgements

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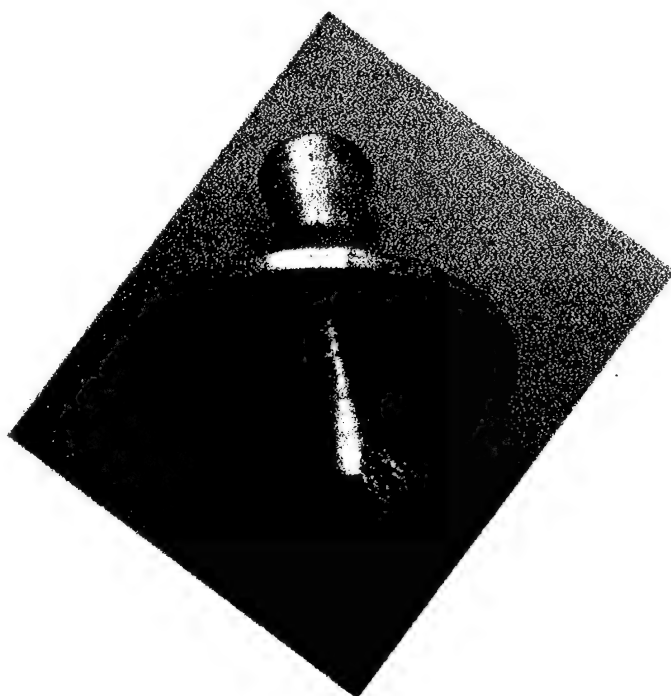


Figure 1 ZrC/W nozzle insert as-received

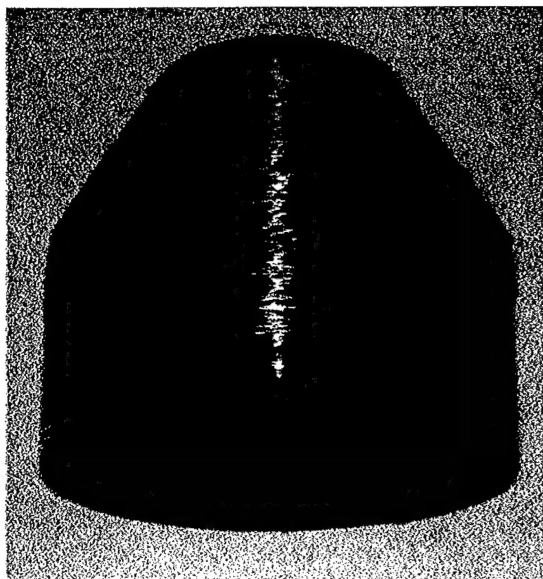


Figure 2. ZrC/W nozzle insert after it has been wrapped with carbon fibers, densified, and machined to size for the test motor

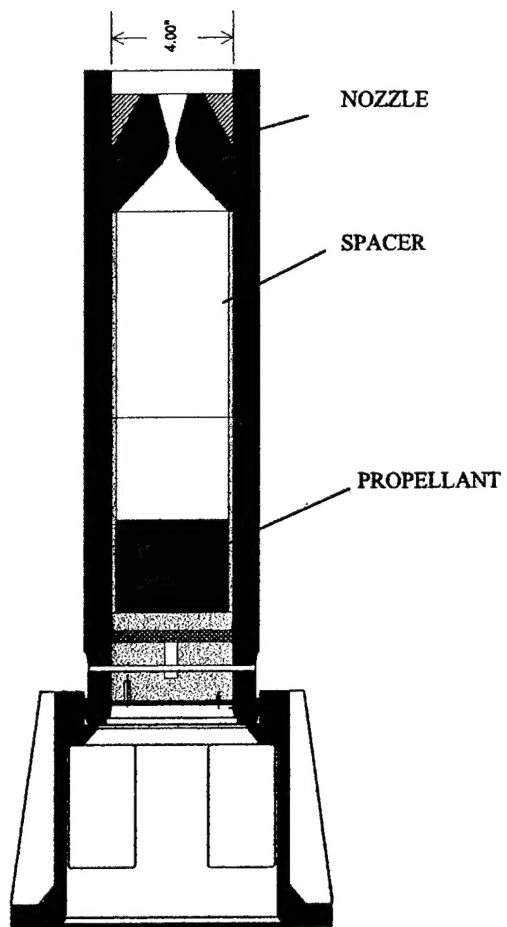


Figure 3. Schematic of Pi-K test motor

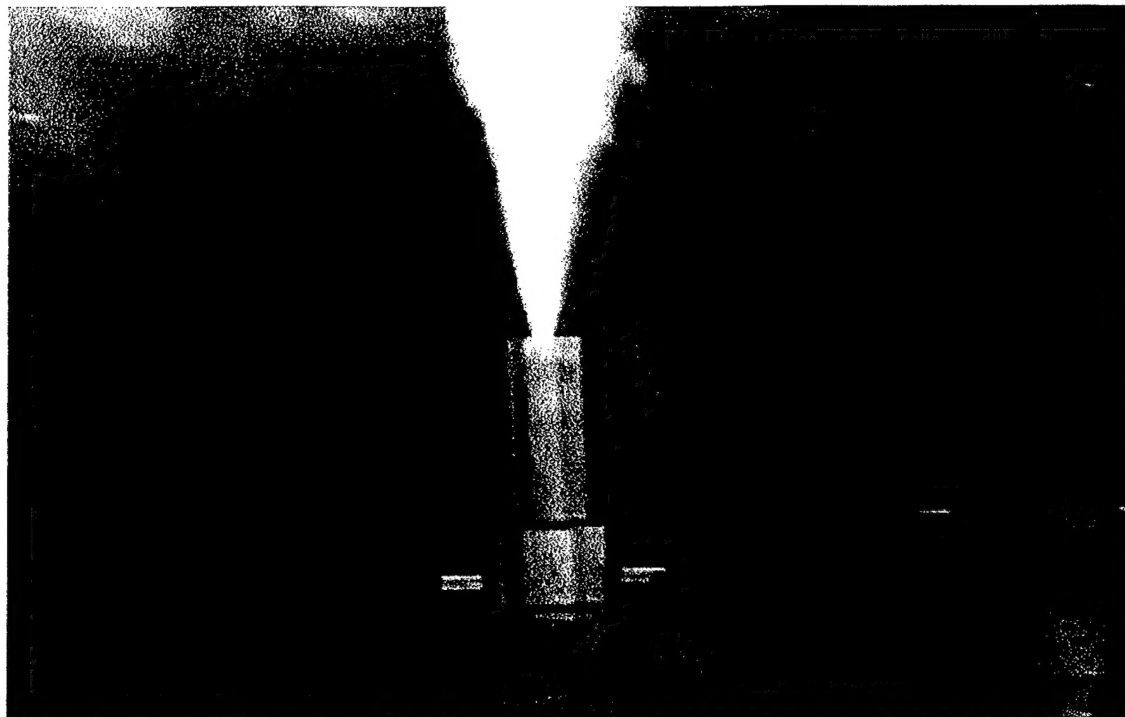


Figure 4. Test Firing of Pi-K motor with carbon-carbon over-wrapped ZrC/W insert

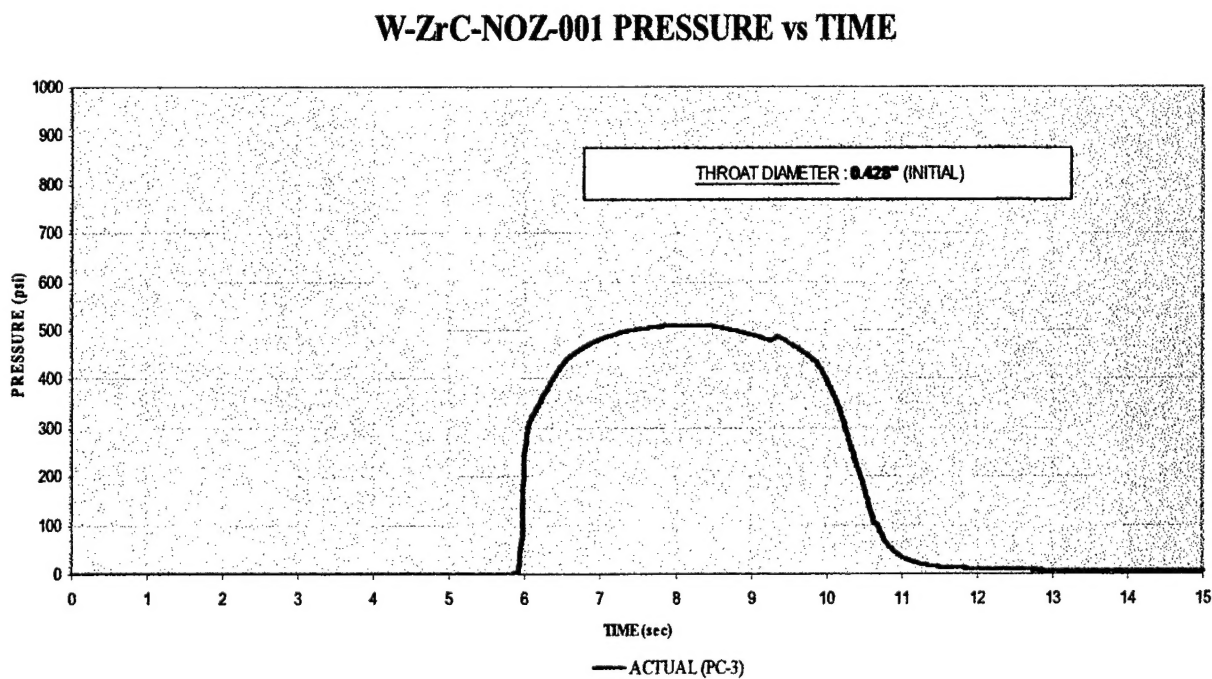


Figure 5. Pressure trace during test firing.

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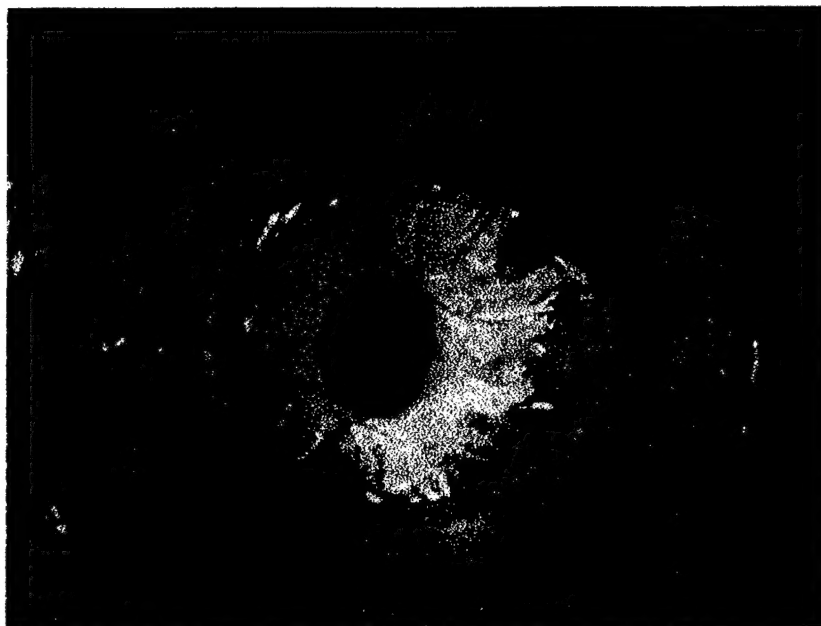


Figure 6. Exit of nozzle showing aluminum oxide deposit on surface of ZrC/W insert that is surrounded by the carbon-carbon composite.